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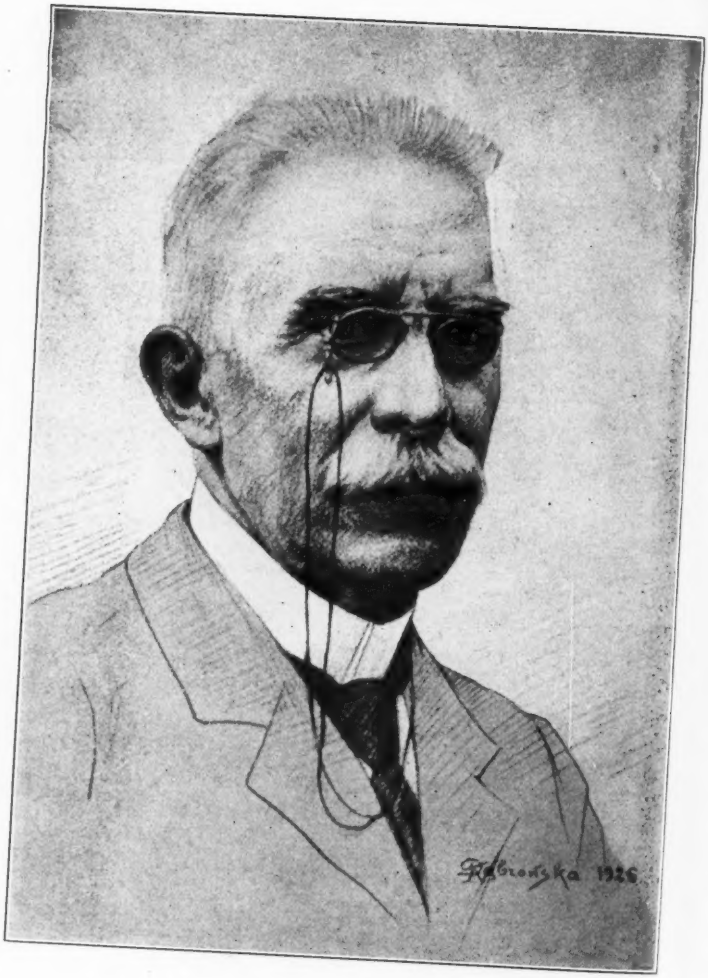


H. Le Chatelier

EDITOR'S OUTLOOK

THE reiteration of principles so fundamental as to incur often the danger of being taken for granted can never be without value, and such emphasis is clothed in additional importance when, as in the article on "The Methodology of Scientific Research" (pp. 2584–9 of this issue of the JOURNAL), it comes from the pen of one who, having tested those principles throughout a more than usually long professional experience, enunciates them with conviction once again in his eightieth year.* The author of this article, Dr. Henry M. Le Chatelier, retired in 1925 from his active professorship in the University of Paris, and is spending a green old age, not in resting from his labors, but in giving to the world the philosophical fruits of his growth in the educational and industrial fields.**

Henry Le Chatelier
1850–

Dr. Le Chatelier's personal contributions to pure and applied science have been many and various. His earliest independent research was concerned with hydraulic materials and was undertaken after his first professional appointment, at the age of 27, to the chair of chemistry at l'École des Mines in Paris. This was followed by a study of the composition and circumstances of formation of various types of minerals, which formed the basis of his later investigations on allotropic transformations, and by a series of researches on the combustion of gaseous mixtures, which resulted in important additions to knowledge on this subject. After his appointment in 1887 as professor of industrial chemistry and general metallurgy at l'École des Mines, he plunged into his work on chemical mechanics, and, proceeding from the previous studies of Berthollet, Sainte-Claire Deville, and Berthelot, he was able to establish the laws of chemical equilibrium by reason of which his name is probably best known in the educational world. In the meantime, he had continued his metallurgical research, in the course of which were contrived the Saladin-Le Chatelier double galvanometer, the metallographic microscope, and the thermo-electric pyrometer, instruments which immediately became indispensable in industry and which placed it on a scientific basis by providing it with reliable measurements.

In 1904, Dr. Le Chatelier established, after some years of effort to secure adequate financial support, the important *Revue de Metallurgie*. He was its first editor and continued in the post until 1920.

Dr. Le Chatelier was prepared by inheritance and training for this influential career. More than one science is represented in his maternal ancestry, and his father was a prominent mine inspector and engineer who contributed largely to the foundations of the French railroads, and who spent his "leisure" in metallurgical work, much in the society of his

* Dr. Le Chatelier's 80th birthday occurred on October 8th of this year.

** See "The Formation of the Élite," J. CHEM. EDUC., 6, 565–71 (Mar., 1929).

intimate friend, Sainte-Claire Deville. It is not surprising that such a father selected science as the most promising field for his sons.

Henry Le Chatelier's earliest training was conducted under the supervision of a mother whose only interest was the education of her children, and when he emerged from childhood, regularity was already so much a part of his character that at nineteen the military discipline at l'École Polytechnique was a matter of course to him, and at the age of seventy he professed himself unable "to appreciate sufficiently the liberty bordering on license, which we enjoy at the Sorbonne." This restraint, so early instilled, carried over into a manhood which thus explains itself: "Order is for me one of the most perfect forms of civilization. I do not envy the independence of the man who zigzags through traffic at the risk of being run down, and hinders the progress of many pedestrians more interesting than himself."

At the age of fifteen, Henry Le Chatelier took a step forward in the world when he was permitted to prepare his lessons daily in his father's private office. Here, under the parental eye, he pursued mathematical courses from his father's records of his own college days. Here he received an informal introduction to the various fields of science through contact with his father's callers, men eminent in civil and industrial life, aspirants to membership in L'Académie des Sciences, soliciting his father's interest, and in these interviews the language of science first became familiar to his ears. He began also to share his father's recreations in his private metallurgical laboratory and to frequent the laboratory of Sainte-Claire Deville, where he met "eminent savants, whose conversations generally took a free enough turn, without much relation to science." But his father took excellent care that the boy should be equally familiar with the work of these men by absorbing their reports to scientific societies and publications, so much so that the son declares it was his complete knowledge of the work of Sainte-Claire Deville which secured his success in the examinations at l'École Polytechnique, which he entered at the age of 19 at the head of his class, and from which he graduated two years later.

His education was now rounded out by five years of practical experience in the Paris School of Mines and the Corps des Mines at Besançon, after which he returned to the School of Mines to take up a teaching career. In 1898 he became professor of mineral chemistry at the Collége de France and a decade later he had the happiness of succeeding Moissan at the Sorbonne in the chair of his own and his father's friend, Sainte-Claire Deville.

Le Chatelier's impress upon the teaching of chemistry has been two-fold. In the first place, he consistently applied his theory that science is one, that its pure and applied forms cannot be thought of as apart, each owing a

constant duty and performing a constant and necessary service to the other. Secondly, he brought about a revolution in method by substituting for the old procedure of studying the elements in single file by property and formula, the more rational method of assembling and presenting chemical facts under the general chemical laws which they illustrate.

Dr. Le Chatelier's extensive services have not passed unrecognized. He is a member of the Institut and Commander of the Legion of Honor. He has frequently been honored with prizes and memberships in distinguished societies of his own and other countries, and his admirers joined in an international tribute to him to celebrate the fiftieth anniversary of his entrance upon a scientific career. On January 22, 1922, a gold medal struck in honor of the occasion was presented to the jubilarian and a purse of 100,000 francs was given in his name to l'Académie des Sciences, of which he has been a member since 1908, by his friends and associates in educational and industrial fields throughout the world. From Dr. Le Chatelier's address of acceptance, we quote the following sentences which give one striking view of what he calls "a particularly happy career": "One makes discoveries when one can, not when one wishes. I have led my entire scientific life without any ambition of this kind, contenting myself with performing each day the duties of my office; in the end I have been generously rewarded."

The JOURNAL OF CHEMICAL EDUCATION *is indebted to Dr. R. E. Oesper of the University of Cincinnati, Cincinnati, Ohio, for the sources of information upon which this sketch is based and for the accompanying portrait of Dr. Le Chatelier.*

Eighth Prize Essay Contest

FUNDS for a prize essay contest, conducted under the auspices of the American Chemical Society, have been provided for the eighth consecutive year by Mr. and Mrs. Francis P. Garvan as a memorial to their daughter, Patricia.

The rules which have been adopted for this year's contest, and which are set forth elsewhere in these pages, are, with two significant exceptions, substantially those which have governed the essay contests in the past. The alterations in regulation provide specific subjects, rather than general topics, for the secondary-school and the normal-school contests as well as for the college contest, and they further provide that all essays to be entered in the contests shall be written under the same supervision which governs the writing of examination papers in the respective institutions at which the contestants are enrolled. Both of these changes are made in ac-

cordance with suggestions received from chemistry teachers by the Prize Essay Committee, and are adopted with a view toward furthering the fundamental aims of the contests.

As we have pointed out heretofore in these columns, the Prize Essay Contests afford the teacher of elementary chemistry an excellent opportunity to motivate the general outside reading which should supplement and humanize the more formal and fundamental portions of the course. In adopting the contest for this purpose it is advisable that the instructor begin to stimulate interest in the essays early in the year. Many students enter upon first courses in chemistry with some knowledge of the contributions which the science has made toward human welfare and with a curiosity to explore the romantic aspects of the subject further. Too often the formal and rather dry subject matter which they encounter is a rude shock to their preconceived notions and tends to blight rather than to nourish the budding interest which they bring to the classroom. Numerous teachers of long and successful experience have found the prize essay work an excellent means of bridging the gap between romance and hard actuality.

Not every teacher cares to make the essay contest a prescribed part of the class work. Some feel that projects of this nature should constitute extra-credit work for ambitious and exceptionally able students. We believe, however, that wherever the teacher feels so inclined, he may very properly assign the preparation of essays as a broadening feature of the course. It is neither possible nor desirable for any textbook to include any considerable quantity of the sort of material which is contained in the popular volumes issued by The Chemical Foundation or in the bibliography recommended by the Prize Essay Committee. The contest provides an incentive to additional reading, and the preparation of an essay constitutes an excellent report upon the intelligence and industry employed in that reading.

Probably, however, there is no one best program which would seem equally desirable everywhere. Perhaps some instructors and institutions will always desire to encourage participation in the essay contests and to aid students in preparing for them, but will prefer, nevertheless, that the contest maintain an extra-curricular status. The one thing to be desired is that teachers may continue to contribute to the success of the contests, as they have in the past, by maintaining a coöperative attitude.

The effects of these contests are impossible to estimate objectively. It is certain, however, that they extend far, in time and space, beyond the generation of students which they directly touch in any one year. Who can say how many friends and supporters of chemistry the contests have made for future years by means of the information disseminated

in connection with them? Who knows how many parents and friends of contestants, many of them influential, have had their eyes opened to the achievements and potentialities of the science through perusal of the essays themselves or the literature employed as an aid in their preparation?

The Fight against Cancer

FOR the second year the New York City Cancer Committee offers to the public its small Christmas memorandum book as a reminder to Shop Early and Mail Early, and asks for contributions of one or two dollars for the support of its work of education. The books will be distributed in the mail, and every one who responds to the appeal will have the satisfaction of sharing in the control of cancer, the great scourge of modern times.

Contrary to general belief, cancer is not an incurable disease. It can, in many cases, be controlled by prompt and proper treatment. This is the message which the New York City Cancer Committee, a local branch of the American Society for the Control of Cancer, is emphasizing by every available means, and in the spreading of which it receives the most cordial and helpful coöperation from the large advertising companies, and from the press. Its symbol, a radiant sword twined with the physician's emblem, over the words "Fight Cancer with Knowledge," is becoming a familiar sight to New Yorkers.

The necessity for this work of public education is shown by vital statistics which indicate a marked increase in the cancer death rate, an increase due partly to better diagnosis and partly to the fact that with improvement in general health conditions more and more persons are reaching the cancer age, that is, thirty-five and over. It is of the utmost importance that the chief signs of the disease should be known so that early diagnosis can be assured, for in this lies the greatest hope of control.

The Committee, therefore, arranges for lectures by physicians conversant with the subject and able to present it in simple form, shows a motion picture giving a simple story, and distributes carefully prepared pamphlets. All of these means—lectures, film, and pamphlets—are designed not to increase but to relieve the fear of the disease which is such a potent factor in causing delay. The work is dependent entirely on voluntary contributions, and the Committee begs for a cordial and generous response to its appeal. Further details of the Christmas sale and free information about cancer, hospitals, clinics, etc., can be obtained by addressing the New York City Cancer Committee, 34 East 75th Street.

THE DIALYZER

1. What French chemist, known to all chemistry for his contributions to the study of chemical equilibria, recently celebrated his 80th birthday? (pp. 2536–9.)

(*For questions* 2–6 *see* pp. 2543–70.)

2. To what is the tan shade of Tussah silk attributed?
3. What is the principal chemical difference between natural silk and the various synthetic fibers?
4. How are metallic rayon fabrics made?
5. What was Chardonnet's contribution to the synthetic fiber industry?
6. Characterize each of the four present commercial processes for manufacturing rayon. Which process produces the least inflammable thread?

(*For questions* 7–9 *see* pp. 2571–83.)

7. Name four types of experiments utilized during recent years for obtaining information on the mechanism of catalytic reactions.
8. From a consideration of recent research, what is the most likely explanation of the mechanism of ammonia synthesis over iron catalysts?
9. In what manner do promoters added to iron catalysts function in the synthesis of ammonia?

(*For questions* 10–11 *see* pp. 2584–9.)

10. To what three qualities does Le Chatelier attribute the success of eminent scientists?
11. State Claude Bernard's rule regarding his adherence to a hypothesis.

12. Has the value of inorganic iodine as a goiter preventive and curative been thoroughly established experimentally? (pp. 2590–9.)

(*For questions* 13–15 *see* pp. 2609–33.)

13. When and by whom was alizarin first isolated from madder?
14. What two German chemists are responsible for the establishment of the structure of alizarin? What is the formula for this dyestuff?
15. What effect did the discovery of a process for synthesizing alizarin have upon the dyestuffs industry in both England and Germany?

(*For questions* 16–18 *see* pp. 2634–44.)

16. What is the purpose of the Bureau of Foreign and Domestic Commerce?
17. Name the three basic fertilizer materials. Compare the United States and Germany in respect to the relative proportions of these three plant foods used.
18. How does the United States compare with the rest of the world with regard to the fertilizer situation?

19. What are the stars? (pp. 2645–54.)

(*For questions* 20–21 *see* pp. 2655–63.)

20. Of what value is Schrödinger's wave equation in the solution of problems in atomic mechanics?
21. What is the significance of Schrödinger's *eigenfunction?*

22. Outline a method for studying, by means of the phase rule, the three-component system: boric acid–tartaric acid–water. (pp. 2675–86.)
23. How would you demonstrate by means of models the relative polarities of ammonia, water, and hydrogen chloride? The reaction of ammonia with water in dissolving and forming ammonium hydroxide, and in ionizing into ammonium and hydroxide ions? (pp. 2687–91.)
24. Is there a reading list available for the teacher of general chemistry who desires to include in his course practical applications of chemical principles? (pp. 2750–7.)

RAYON—TODAY AND TOMORROW

ROBERT E. HUSSEY AND PHILIP C. SCHERER, JR., VIRGINIA POLYTECHNIC INSTITUTE, BLACKSBURG, VIRGINIA

Ever since the days of the Garden of Eden mankind has been interested more or less in fabrics of either animal or vegetable origin. We are still copying, in a way, the procedure of that day, only using *mulberry leaves*, and at present are fashioning our fabrics from the stalk fibers and even from the wood itself. The most important textile fibers at the present time are linen, wool, cotton, silk, and rayon.

Some of the very oldest fabrics which are in existence come from the tombs of Egypt. These were undoubtedly the clothing of those early people and were also used as mummy wrappings. These fabrics are composed of linen, a vegetable fiber obtained from the flax plant. Presumably Egyptian linens occupied at that time a reputation similar to that in which Irish linens are held at the present time.

Wool was unquestionably known and used at this time. Quoting from Glazier's book (*1*):

> Herodotus says, "Egyptians wear a linen tunic fringed about their legs and called calasure, over which they wear a white woolen garment; nothing of woolen, however, is taken into the temple or buried with them, as their religion forbids it."
>
> Apuleius says, "Wool, the excretion of a sluggish body, taken from a sheep, was deemed a profane attire even in the times of Orpheus and Pythagoras; but flax, that cleanest production of the field, is rightly used for the most inner clothing of man."

Thus we can understand why we find no woolen fabrics in the tombs of the Egyptians, although it was used as an article of clothing. We also see that linen occupied the aristocratic position among the early fibers until the introduction of silk.

Cotton, a vegetable fiber, was known during the early Chinese dynasties and seems to have been classified by them as "tree wool." It was not until about 1364 A. D. that the extensive cultivation of it was taken up in several of the Chinese provinces. India assumed the lead in the production of cotton and held this position up to the sixteenth century.

If wool was regarded in early times as being profane, certainly the product from the lowly silkworm would have been placed even lower down in the scale but for the exalted pedestal upon which it was placed by the Chinese—if the many early legends regarding its introduction are correct. Most of these legends place the origin of silk in China and attribute the discovery and start of the silk industry to royalty.

Perhaps one of the most interesting and fascinating of the many legends is the one about the little daughter of Emperor Fu-hi. This diminutive representative of the royal family was playing house in her playground and was acting as hostess at a tea given in honor of her royal ancestors. Several of these ancestors, represented by cocoons of the silkworm, were carefully

reposing upon an altar in front of which she placed a steaming hot cup of tea. In some unaccountable manner one of the "ancestors" rolled off the altar into the tea. Horrified by this tragedy, neither the little hostess nor her mother could do anything and, in the meantime, the cocoon simply soaked and softened in the steaming tea. Finally, one of the maids rescued the unlucky "ancestor" but in so doing noticed that great lengths of a fine silky filament could be unwound. Thus the cultivation of the silkworm and the production of silk fabrics became a royal industry which remained a Chinese secret for about four hundred years.

The most important variety of silkworm at present is the *Bombyx mori*. This species maintains its lead in value and importance from the centuries of its cultivation. A wild variety known as the Tussah moth produces the Tussah silk. The tan shade of this silk is attributed to the fact that these caterpillars feed on oak leaves.

EMPEROR FU-HI'S DAUGHTER

While most of the silk produced comes from China, Japan, and India, there seems to be no reason why a natural silk industry should not be developed in the United States. To do this would require a considerable amount of study and research. Along this line the authors wish to mention the "Book of the Silkworm," by Susan Minns, published by the National American Society of New York. This book gives a brief but exceedingly interesting account of sericulture and points out various possibilities among our native species.

The silk filament is composed of two parts: one is sericin, the silk glue, which holds together the two tiny fibroin filaments which compose the second part. The nature of fibroin is receiving much attention from chemists at the present time. Efforts are being made to determine if possible just what it is. We know that it is a protein and under certain chemical treatment breaks down principally into three amino acid residues. The

amino acids all contain nitrogen. This is one of the principal differences chemically between natural silk and the various synthetic fibers.

Properties

Silk is distinguished by its great strength and elasticity. In the pure unweighted state, silk is lighter than linen, cotton, or rayon. It is hygroscopic and will absorb up to 30 per cent of moisture and still have a dry feel and appearance. With increase in moisture there is a slight decrease in its strength and elasticity. It has a soft appealing luster and a peculiar property called "scroop," which is a characteristic crackling or rustling sound produced when the fibers are squeezed and pressed.

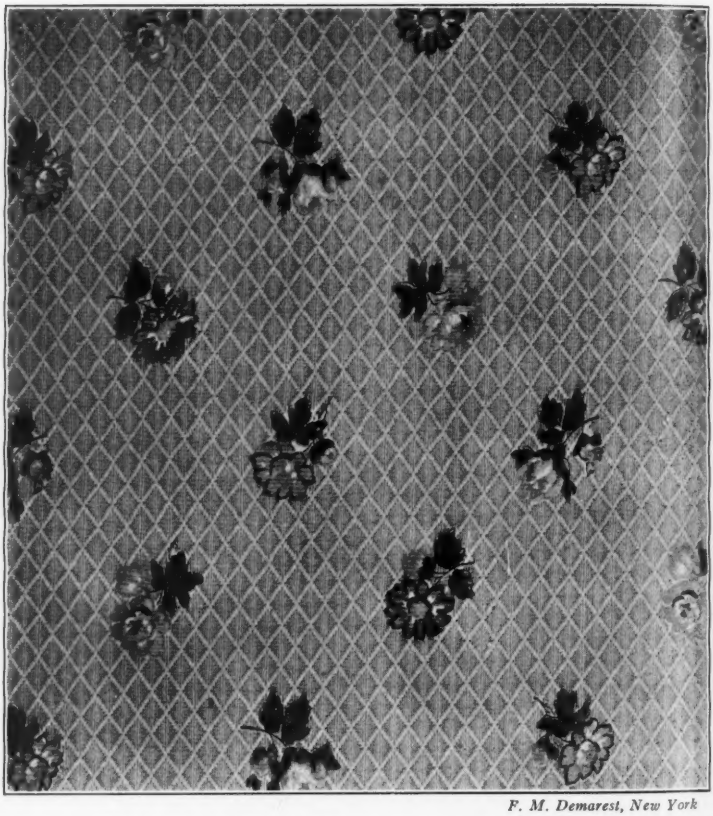
It was the idea of obtaining a thread having these desirable qualities in much greater amount and at much less expense that started chemists out on their efforts to obtain an "artificial silk." While unsuccessful in producing a real artificial silk, the synthetic fiber that has been produced is valued now on account of its own peculiar properties.

Rayon is usually more lustrous than silk. This, however, is not a safe criterion as low-luster rayons are being produced. Also a high-luster rayon can be delustered to any desired state. As a rule they are slightly weaker and show a little less elongation than natural silk threads. The strength is being improved constantly and it is now possible to make rayon by special methods of spinning, which will be stronger when wet than natural silk. Claims have been made recently for a special synthetic fiber that will stand rubbing when wet. Most of the rayon loses about one-half of its strength when wet and while in this condition must be handled very carefully as the threads are very tender. When dried, however, they regain their strength.

Fabrics

The textile art had been more or less at a standstill for some time until it received a stimulus from the introduction of rayon. The combinations, using the basic textile fibers, had been pretty thoroughly worked out. Changes in the type of fabric by new combinations of the various fibers were few. A study of the old fabrics shows that the very early weavers were exceedingly skilful in the production of fine and beautiful materials for useful and ornamental purposes.

The development of rayon gave the textile world a new fiber, thus opening up the entire fabric field. New combinations and types of fabrics have been appearing constantly. We have fine fabrics woven from rayon alone and others where rayon is used for mere decorative purposes. Acetate rayon takes the dyes differently from the others and invariably requires a different type of dye. Thus by the proper combinations of the



F. M. Demarest, New York

SLIP COVER MATERIAL, COTTON WARP AND RAYON FILLING

different types of synthetic fibers with cotton, silk, wool, and even linen, very pleasing effects can be obtained by the different methods of dyeing.

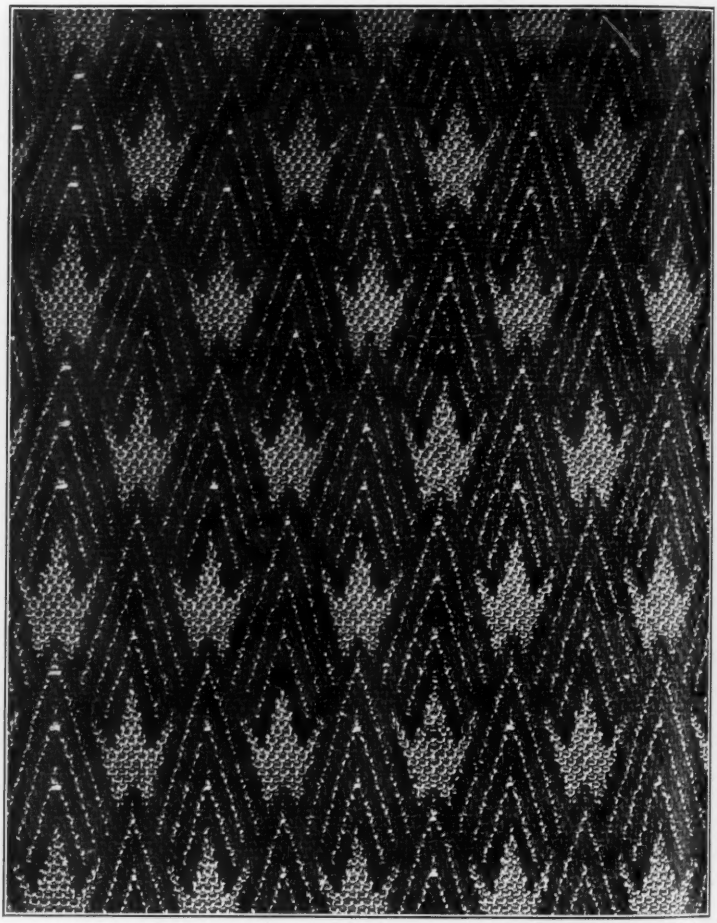
It is impossible in the scope of this article to go into all of the uses which have been or may be made of rayon. In regard to the future, it is interesting to note that Doctor Charles E. Mullin states (*2*) that the world's production of rayon for 1929 was less than 3 per cent that of the natural fibers.

The original cloth of gold was woven from gold threads. These threads were made, according to the earliest account given in the Book of Exodus, by beating the metal into thin plates and then cutting these plates into wires. To quote again from Glazier's book:

> A record of the death of Anne, Queen of Richard II, states that the "Herec" was covered with cloth of gold, which was afterward sold for 66£.

F. M. Demarest, New York

CLOTH OF RAYON WARP AND CORDED COTTON FILLING



F. M. Demarest, New York

AUTOMOBILE UPHOLSTERY CLOTH, RAYON AND WOOL

Cloth of gold may now be worn by a person in the most ordinary circumstances. Metallic rayon fabrics are made today by two different methods. In one method the rayon thread is subjected to a suspension of finely divided metal in a liquid or mixture of liquids which soften the thread somewhat. The small flakes of metal become attached to the soft sticky thread and as the solvents evaporate the metal firmly adheres. Cloth of this type carries the metal on the surface of the thread and thus is not permanent. Continued washing of the fabric gradually wears away the metal.

du Pont Rayon Co.

CLOTH OF COTTON WARP AND RAYON FILLING

The second method of preparation gives a cloth that will wear much longer. By this method the metal in the finely divided state is introduced directly into the solution to be spun. Thus the tiny metal flakes are well distributed not only along the surface but throughout the entire thread. This gives a metal cloth which lasts as long as any rayon thread remains. Thus we may have cloth of gold or silver at a more reasonable price than formerly.

The statement is often made that one can readily distinguish a rayon fabric from one made of natural silk. This might have been the case several

years ago, but it is exceedingly difficult at present. Now even an expert must withhold his decision in many cases until he has submitted the fabric in question to special tests. There are several reasons for this. The synthetic fibers have been improved wonderfully by the enormous amount of research work which has been done and is still being conducted with the object of improving the product. It is not uncommon to hear people remark now that some rayon article has given them much better service than a silk one.

In 1770 Dubet, a French scientist, described experiments by which he produced filaments from a solution obtained by extracting the silky gum from dead silkworms. This same thing is done today. The broken and damaged silk cocoons are also dissolved and by using this solution to coat a fine cotton thread we have a silk thread with a cotton center.

Instead of using a solution of natural silk for "plating," cotton or other fibers may be coated with rayon. The textile people sometimes double or triple their yarns before weaving. In this way we may find any and all combinations of the basic fibers in the same thread. We may illustrate doubling in this way. Suppose we take a thread of natural silk and one of rayon and twist them together. The result will be a larger thread which will be half rayon and half silk. If the natural silk thread had been larger than the one of rayon our result would have consisted of over half natural silk. How would a fabric made from threads of this type be classified? As natural silk or as rayon?

The trend has been to produce finer synthetic threads which also have a much higher filament count. This produces a much softer product and one which resembles silk more closely. A new and very novel use of rayon has just been made public. This is the use of the very fine rayon filament produced by the Bemberg Corporation of America to prepare an artificial spider's web. Two dozen of these rayon cobwebs (see page 2551) were prepared by the Bemberg Corporation for decorative purposes in the restaurant "Old Algiers," established by William Childs at Broadway and 102nd Streets, New York City. The filament from a natural spider's web measures about 0.00023 of an inch in diameter while the Bemberg filament measures 0.0004 of an inch. We wonder what the next developments will be.

Early Stages of Development

An account of the gradual development of the rayon industry from its conception to the present-day production is exceedingly interesting. It gives an idea of the amount of investigation and study which has been contributed by a great many scientists and inventors in placing this industry upon a firm foundation. Opinions seem to differ somewhat as to the person first suggesting the possibility of producing threads artificially. Sir William Bragg, in a lecture at the Royal Institution (*3*) states that the idea of

Photo by Joel Feder

RAYON COBWEB

producing artificial silk was first mentioned by Robert Hooke in 1665. Hooke suggested (*4*) in his "Micrographia":

> There might be a way found out to make an artificial glutinous composition much resembling, if not full as good, nay better, than that excrement or whatever other substance it be out of which the silkworm wiredraws his clew.

Others state (*4*) that de Reaumur, a French physicist and naturalist in 1734 made the suggestion in his "*Memoire pour servir a l'Histoire des Insectes*" similar to the above. In 1842 Schwabe read a paper before the Manchester meeting of the British Association of Silk Manufacturers suggesting the idea of extruding certain solutions through fine holes. Audemars of Lausanne, Switzerland, took out the first English patent in 1855. This covered drawing nitrocellulose threads out of an ether-alcohol solution by means of a steel pointer and reeling them up.

Without doubt the greatest advance of that time was made by Count H. de Chardonnet, a highly trained and skilful French scientist. Chardonnet had been conducting some research work on the diseases of the silk worm and had been much interested in the fact that they ate the cellulose contained in the mulberry leaves and shortly afterward spun their cocoon out of fine lustrous filaments. A little later, while working on guncotton for

the French Government, he was struck by the luster on the surface of the small sticks of guncotton. He proceeded to investigate and in 1884 presented an account of his work to the *Académie des Sciences*. He took out patents covering his process and machinery in 1885. In 1889 he exhibited gowns made from his "silk" at a banquet. Unfortunately, the threads were not denitrated and therefore were highly inflammable, thereby making them useless. The only difference between Chardonnet's first threads and guncotton was in the physical size. Think of a hunter loading his shotgun with small pieces of this artificial silk, yet he would have obtained just as good results as if he had used smokeless powder. Women are not anxious to wear dresses which may leave them upon the slightest provocation. Even though some of them might wish to convey the impression of flaming youth they would hesitate before taking a chance of an actual demonstration.

What would be more natural than for the chemist to destroy this instability? Since he had created a kicking mule it was up to the inventor to denature the beast. This he finally did by denitrating his silk. The success of his research work on this problem may be judged by the fact that Chardonnet process rayon today is rated by the Government bureau at Washington as one of the least inflammable. It burns at the same rate as a corresponding thread of cotton. Chardonnet's name will always occupy a very important place in the rayon industry.

Louis Henri Despaisses, in 1890, making use of Schweitzer's discovery (1857) that an ammonia solution of copper oxide had the power of dissolving cotton, took out patents for making rayon by the cuprammonium process. Nothing much was done with this process until seven years afterward when Pauly's work placed it on a commercial basis.

While investigating cellulose, Cross, Bevan, and Beadle discovered that cellulose treated with strong caustic soda would react with carbon disulfide under proper conditions to give an orange-colored product which was soluble in water. This discovery in 1891 led to the development of the viscose process.

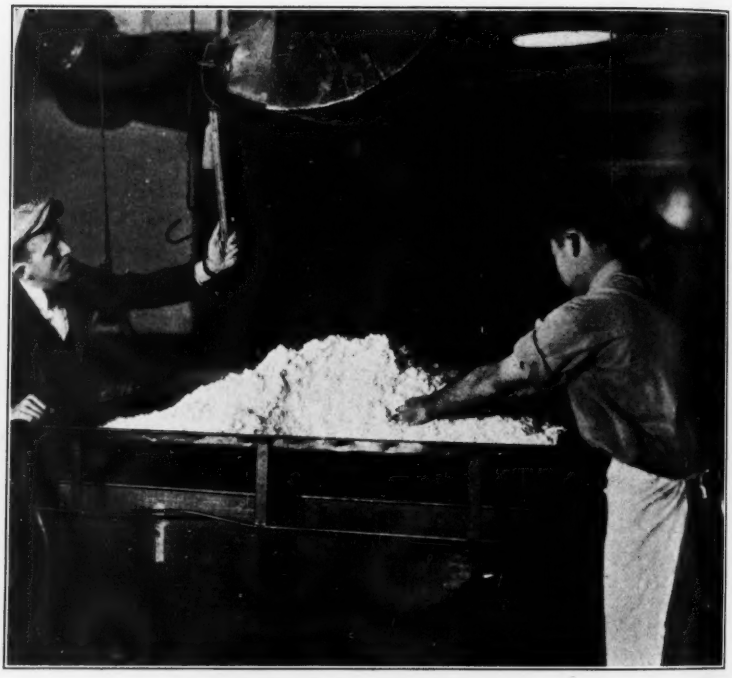
Although cellulose acetate was discovered as early as 1869 by Schutzenberger and Naudin, its use for the production of rayon has been emphasized only recently, chiefly through the work of Henri Dreyfus and others.

Manufacturing Processes

The actual production of rayon is really much the same as the method employed by the silkworm for making natural silk. Suppose we pause for a moment to consider what takes place from the mulberry leaf to the finished cocoon spun by the worm.

The mulberry leaf is made up essentially of cellulose, a carbohydrate composed chemically of carbon, hydrogen, and oxygen. The silkworm chews

Count Hilaire de Chardonnet
1840-1924



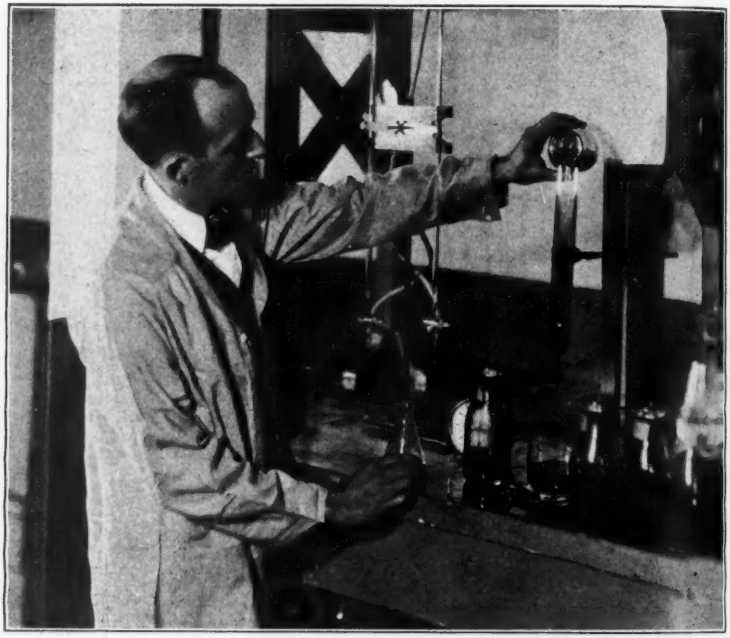
"CRUMBS" IN HUMIDITY ROOM

up mulberry leaves and digests the cellulose and then stores up a secretion in two little silk glands which lie lengthwise of the body. When the worm is ready to spin its cocoon, a tiny thread from each gland passes out through a small hole at the head where they are united and held together by a silk glue, sericin, also secreted by the worm. The worm by a figure-8 motion of its head gradually spins its cocoon.

In the production of rayon the starting point is a high-grade cellulose, usually in sheet form, for convenience. This cellulose then undergoes some special treatment which we may call "digestion" as well as any name. It is finally obtained in solution and is stored in large tanks. These storage tanks, filled with the cellulose solution, may be likened to the silk glands of the silkworm. The next step in the rayon process is to force the cellulose solution out through an arrangement of fine holes called the spinneret. In some cases the threads are coagulated merely by contact with the warm air, in others the thread is "set" by passing through a liquid "setting bath." The coagulated threads are wound up and washed and then receive the proper finishing treatment before being packed for shipment. Before at-

Wm. Shewell Ellis, Philadelphia

VISCOSE STORAGE TANK AND RIPENING ROOM



Wm. Shewell Ellis, Philadelphia

LABORATORY DETERMINATION OF THE VISCOSITY OF VISCOSE SOLUTION

tempting to discuss in detail the four present commercial processes, it might be well to give a little idea of the preparation and chemistry of the most important raw material, namely cellulose. The two varieties which are used for the production of rayon are cotton linters and sulfite wood pulp.

Linters are the very short fibers which remain with the seeds when these latter are removed from the long staple cotton. By giving the seeds what really amounts to a close shave we have the product known as linters. The ordinary "saw gin" is capable of treating 5000 to 6000 kilograms of seeds in ten hours and recovers 160 to 180 kilograms of linters. They are oily and impure and are first subjected to an extraction process which frees the fibers from fat, wax, and oil. Next they are given a short boil in weak alkali solution under slight pressure, then washed, bleached, rewashed, and dried. It is often necessary to lower the iron content of the linters which are to be used for rayon production as the presence of iron greatly interferes with the quality of the product, especially in the viscose process. This may be done by an oxalic acid treatment after the bleaching.

The question of wood pulp is a little more exacting. Only wood pulp produced by the sulfite process is looked upon with favor and this must be

given a special treatment, the so-called "alpha treat," before it is acceptable.

Chemists have been studying cellulose for a long time and have found out considerable about it, and yet we are really working more or less in the dark when we use it. We know it is composed of carbon, hydrogen, and oxygen the same as sugar or starch and yet it differs from these in some way. The layman probably has obtained the idea by this time that the word "alcohol" means only one of two things; either something definitely connected with prohibition, or on the other hand, "wood" alcohol, or to use its chemical name, methyl alcohol, something connected with blindness. It might have been more fitting if we had placed the blindness before the prohibition since in the long series of alcohols methyl really should precede ethyl.

Alcohols as a *class of compounds* are exceedingly important and necessary in our scheme of life. Glycerin, sugars, starches, and even cellulose are a few illustrations of other alcohols. Suppose we illustrate our alcoholic reactions by the use of glycerin. If we treat glycerin with what is known as a fatty acid we obtain an "ester." The chemical reaction can be written in this way:

$$\begin{array}{lcl} CH_2OH & CH_3COOH & CH_2OOCH_3 \\ | & & | \\ CHOH + & CH_3COOH = & CHOOCCH_3 + 3H_2O \\ | & & | \\ CH_2OH & CH_3COOH & CH_2OOCCH_3 \end{array}$$

glycerin + 3 acetic acid = glycerin triacetate + 3 water

If we use a mixture of nitric and sulfuric acids in place of the acetic acid above we will get glycerin trinitrate which is erroneously but commonly called nitroglycerin. By using special acids such as palmitic, stearic, or oleic to combine with glycerin we obtain our fats or oils.

We can reverse the above reactions if we select the proper conditions. If we take a fat, lard for instance, and boil it with caustic soda (soda lye) we break up the "ester" and get back our glycerin and palmitic acid. The latter will be present as a sodium salt which we know better as soap.

$$\text{Fat} + NaOH = \text{glycerin} + \text{soap}$$

Cellulose behaves in practically the same way as glycerin, only since cellulose is a much more complicated alcohol its reactions are somewhat more difficult to carry out.

We are now ready to take up the different processes for making rayon, and keeping the above chemical explanations in mind should simplify what follows.

Chardonnet or Nitrate Process

In the process developed by Count de Chardonnet, we start by taking purified cellulose and treating it with the proper mixture of nitric and

Du Pont Rayon Company Plant Manufacturing Acele and Commercial Cellulose Acetate, Waynesboro, Virginia

Wm. Shewell Ellis, Philadelphia

INSPECTION OF RAYON CAKES

sulfuric acids and obtain cellulose trinitrate. The trinitrate, which is also called nitrocellulose, is practically insoluble in a mixture of ether and alcohol. It forms the guncotton which is used for the manufacture of smokeless powders. By the proper adjustment of the composition of the mixed acid and the temperature and time of nitration we can control somewhat the percentage of nitrogen introduced into the cotton, thereby giving us lower nitrates of cellulose which are soluble in an ether-alcohol mixture.

The lower nitrates, known technically as "pyroxylin" cottons, are used in the production of ivory substitutes, spirit lacquers, and rayon. After nitration these lower cellulose nitrates are washed thoroughly in cold water and then passed into a beater which cuts the fibers into shorter lengths, thus aiding in the complete removal of the acids and any sulfates

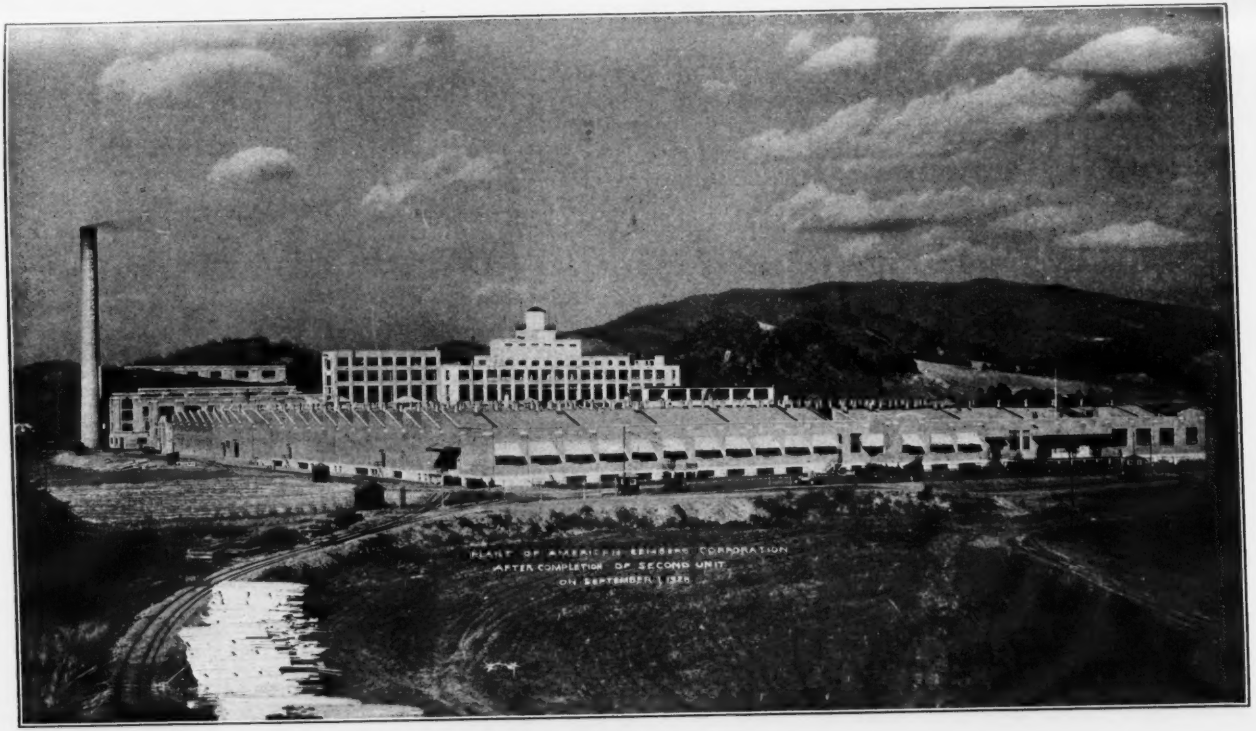
which may have been formed. This is a great help in producing a stable product. Excess moisture is removed and the nitrate is dissolved in a mixture of ether and alcohol. This collodion solution, containing from 15 to 25 per cent cellulose nitrate, is carefully filtered and de-aerated and then forced through the spinneret. This consists of a number of glass capillaries, the number corresponding to the number of filaments desired in the particular thread. The filaments which are extruded from the spinneret pass through a chamber of warm air, during which time the solvents evaporate and the hardened thread forms. The thread may be wound up on a bobbin (bobbin spinning) or may be collected in a centrifugal pot (pot spinning).

The after-treatment of the thread depends upon the type of spinning used. If it has been collected by bobbin spinning, the filaments must be twisted together, whereas in the pot-spinning method the thread is already in the twisted form. There remains then only the denitration process, washing, finishing, and drying. The denitration is accomplished usually in the skein by means of a solution of sodium hydrosulfide, after which the product is thoroughly washed, bleached, rewashed, and dried. By denitrating our thread we change our cellulose nitrate back to cellulose, giving what is known as a "regenerated cellulose" rayon. As complete recovery of the solvents used as possible and recovery of the spent acids are of vital importance in this process. The Tubize brand and the Chardonnize brand (low-luster) are the only rayons made in this country by this process.

Cuprammonium Process

This process makes use of the fact that an ammoniacal solution of copper oxide has the power to dissolve cellulose. The cuprammonium solution is prepared by dissolving copper hydroxide in a strong ammonia solution. To this the moist purified linters are added. The cuprammonium cellulose solution thus formed is filtered and de-aerated and is then ready for spinning. The spinnerets in this case are generally constructed of nickel and contain a number of holes, usually a trifle larger than used in the other methods. The spinneret is immersed in either an acid or alkali "setting bath" which causes a slow coagulation of the filaments. During this coagulation the threads are subjected to tension which stretches them out, thereby producing finer filaments than is generally possible in the other processes. The final hardening of the stretched filaments is accomplished by using a second setting bath. By means of this "stretch spinning" method it is possible to produce filaments at least twice as fine as those of natural silk.

The yarn at this point is contaminated by considerable amounts of copper which is removed by dipping the skeins in a solution of dilute sulfuric acid. They are then washed, neutralized, bleached, and finished. There


PLANT OF AMERICAN RUBBER CORPORATION
AFTER COMPLETION OF SECOND UNIT
ON SEPTEMBER 1, 1928

are only three concerns in this country using this process today. These are the American Bemberg Company of Elizabethton, Tennessee, The Furness Corporation of Gloucester City, New Jersey, and the Rosland Corporation of Paterson, New Jersey.

Viscose Process

About 82 per cent of the total production of rayon today is made by the viscose process. The first step consists in soaking the sheets of cotton or wood pulp in a strong solution of caustic soda. The excess is then pressed out and the swollen sheets of "alkali cellulose" are then torn into fine "crumbs" in what is known as a shredding machine. These "soda cellulose crumbs" are then placed in sheet-iron cans, covered and "aged" for a definite length of time under very carefully controlled temperature and humidity conditions. After the proper aging they are treated with carbon disulfide in drums or churns called "xanthators," forming the compound known as sodium cellulose xanthate which is then dissolved in dilute caustic soda solution and gives the solution known as "viscose." This viscose solution must be "ripened," *i. e.*, allowed to stand at a carefully controlled temperature for a definite time. When ripe the viscose sirup, which in appearance very closely resembles molasses, is filtered, de-aerated, and spun through metal spinnerets into an acid "setting bath." In this acid-bath the sodium cellulose xanthate compound is broken up, and thus the cellulose filaments are regenerated. The filaments are collected from this bath by either the bobbin- or pot-spinning method. The threads are then desulfurized by treating with a solution of sodium sulfide after which they are bleached and finished.

Acetate Process

This is the most recently developed of the four processes and in some respects resembles the Chardonnet method. Cellulose is treated with acetic anhydride in the presence of acetic and sulfuric acids. The sulfuric acid acts as a catalyst to aid in the formation of the cellulose triacetate which is soluble in glacial acetic acid. The triacetate is subjected to a partial hydrolysis, thereby converting it nearly to the diacetate which is precipitated with water, washed free from acid, dried and dissolved, usually in acetone, although other organic solvents may be used.

After filtering and de-aerating, the solution is spun into a long, narrow chamber where the solvent is removed by a current of warm air. The separate filaments are collected and twisted and the yarn finished for shipment. In this process the yarn remains as cellulose acetate and therefore has different properties from the regenerated rayons.

It may be noticed that apart from the acetate process, the rayon is made by starting with a cellulose base. This is modified in various ways, changed

SKEIN INSPECTION

into new compounds which are soluble in various solvents, spun into threads, and then changed back to the cellulose base. While we will make use of the Chardonnet process to illustrate our story it can be applied to the other methods as well. An efficiency expert with no chemical training was sent to an official of one of the rayon companies to obtain a general idea of how synthetic fibers were made. After listening to the explanation he replied in great disgust, "This is the most inefficient manufacturing process I ever heard of. How do you expect any one to invest in a process where there is so much waste of time and chemicals? You simply nitrate so that

DU PONT VISCOSE PROCESS RAYON COMPANY, RICHMOND, VIRGINIA

you can denitrate and you dissolve so that you can evaporate the solvents later."

Possibly if this efficiency expert would carry out a little research work he might find a suitable solvent which would dissolve cellulose and thus simplify our process.

Miscellaneous Fibers

There are at present a number of products which might be classed as miscellaneous fibers. These are interesting and are all made by slight variations in some of the regular methods for rayon production. The hollow filament seems to have been received with favor abroad but is known very little in this country. This is a regular viscose thread but in spinning certain modifications are made to introduce air or gas into the center of each filament. By proper treatment afterward this hollow tube collapses as the gas is removed. The tendency is to produce a lighter, softer thread and one that it is claimed has more covering power and is warmer than the regular thread. Research is in progress to produce hollow filaments with the other types of synthetic fibers.

Artificial horsehair ("monofil") may be produced by using a spinneret containing only one hole. The strand of "horsehair" is about the size of the

ordinary rayon thread. If the opening in the spinneret be a long, narrow slit, then we have a flat, ribbon-like material. This artificial straw is much used at present in the making and trimming of ladies' millinery.

By allowing a viscose sirup to flow out through a long, narrow slit into a setting bath, sheets of regenerated cellulose may be formed (5). This cellophane, made by the du Pont Cellophane Company, is used wherever a transparent wrapping paper is desirable or aids in presenting an attractive package. It is especially used in wrapping foodstuffs.

Artificial wool is another interesting synthetic fiber. This is generally made from low-luster or delustered material and in most cases has a slight definite curl imparted to it. The synthetic wool compares quite favorably with natural wool in finish and appearance, but the synthetic product does not retain warmth like the natural wool.

Production

Although a comparatively young industry, the capital invested today in the United States alone is probably well over $200,000,000. The domestic production for 1930 is estimated at 162,350,000 pounds, which at the rate of $1.15 a pound would place the value of $186,702,500 upon the rayon made in the United States this year. The estimated world production for 1930 is placed at approximately 462,500,000 pounds.

Table I and Figure 1 (pages 2566 and 2567) show the location in the United States of the different companies with their estimated 1930 capacity and the type of yarn that they produce.

Table II gives an idea of the distribution of the domestic production by states.

TABLE II

Estimated Production of Rayon for 1930 by States

State	*Pounds*	*% U. S.*	*% World*
Pennsylvania	46,000,000	28.30	9.95
Virginia	45,000,000	27.80	9.80
Tennessee	27,500,000	16.90	5.94
New York	9,700,000	5.96	2.09
Maryland	8,000,000	4.94	1.73
Georgia	6,200,000	3.80	1.34
North Carolina	5,500,000	3.40	1.09
Ohio	5,500,000	3.40	1.09
Other States (5)	8,950,000	5.50	1.94
Totals	162,350,000	100.00	34.94

Let us consider for a little what an industry of this size would demand in some of the necessary chemicals. The domestic consumption of 50° Bé. sulfuric acid amounts to approximately 145,000 tons. Last year 105,000

TABLE I

United States Production

Company	*Plant location**	*Started production*	*Process*	*Ownership*	*Estimated capacity 1930*
Acme Rayon Corp.	Cleveland, Ohio 1	1924	Viscose	100% U. S.	1,100,000
American Bemberg Corp.	Elizabethton, Tenn. 2	1927	Cupra	Over 51% German	4,000,000
American Enka Corp.	Asheville, N. C. 3	1929	Viscose	Less than 5 % U. S.	5,000,000
American Glanzstoff Corp.	Elizabethton, Tenn. 4	1928	Viscose	Over 51% German	9,000,000
Amoskeag Mfg. Co.	Manchester, N. H. 5	..	Viscose	100% U. S.	1,000,000
Belamose Corp.	Rocky Hill, Conn. 6	1925	Viscose	100% U. S.	1,500,000
Celanese Corp. of America	Amcelle, Maryland 7	1925	Acetate	....	8,000,000
Delaware Rayon Corp.	New Castle, Delaware 8	1927	Viscose	100% U. S.	2,000,000
Du Pont Rayon Co.	Buffalo, N. Y. 9	1921	Viscose	100% U. S.	28,000,000
	Old Hickory, Tenn. 10		Viscose		
	Richmond, Va. 11		Viscose		
	Waynesboro, Va. 12		Acetate		
Furness Corp.	Gloucester City, N. J. 13	1930	Cupra	100% U. S.	(3,600,000 planned)
Hampton Co.	Easthampton, Mass. 14	..	Viscose		
Industrial Rayon Co.	Cleveland, Ohio 15	1921	Viscose	100% U. S.	10,000,000
	Covington, Va. 16		Viscose		
A. M. Johnson Rayon Mills	Burlington, N. C. 17	1930	Viscose	100% U. S.	(14,400,000 planned)
Napon Rayon Corp.	Clifton, N. J. 18	..	Cupra	100% U. S.	
Neidich Viscose Corp.	Burlington, N. J. 19	..	Viscose		
New Bedford Rayon Co.	New Bedford, Mass. 20	1929	Viscose	100% U. S.	2,000,000
Rosland Corp.	Paterson, N. J. 21	1930 (?)	Cupra	100% U. S.	
Skenadoa Rayon Corp.	Utica, N. Y. 22	1928	Viscose	100% U. S.	3,250,000
Tubize-Chatillon Co.	Hopewell, Va. 23	1921	Nitrate	100% U. S.	17,500,000
	Rome, Ga. 24	1929	Viscose		
			Acetate		
Viscose Company	Marcus Hook, Pa. 25	1911	Viscose	15% U. S.	70,000,000
	Lewistown, Pa. 26		Viscose	85% English	
	Meadville, Pa. 27		Acetate		
	Parkersburg, W. Va. 28		Viscose		
	Roanoke, Va. 29		Viscose		
Woonsocket Rayon Co.	Woonsocket, R. I. 30	1930	Viscose	100% U. S.	

* See map, Figure 1.

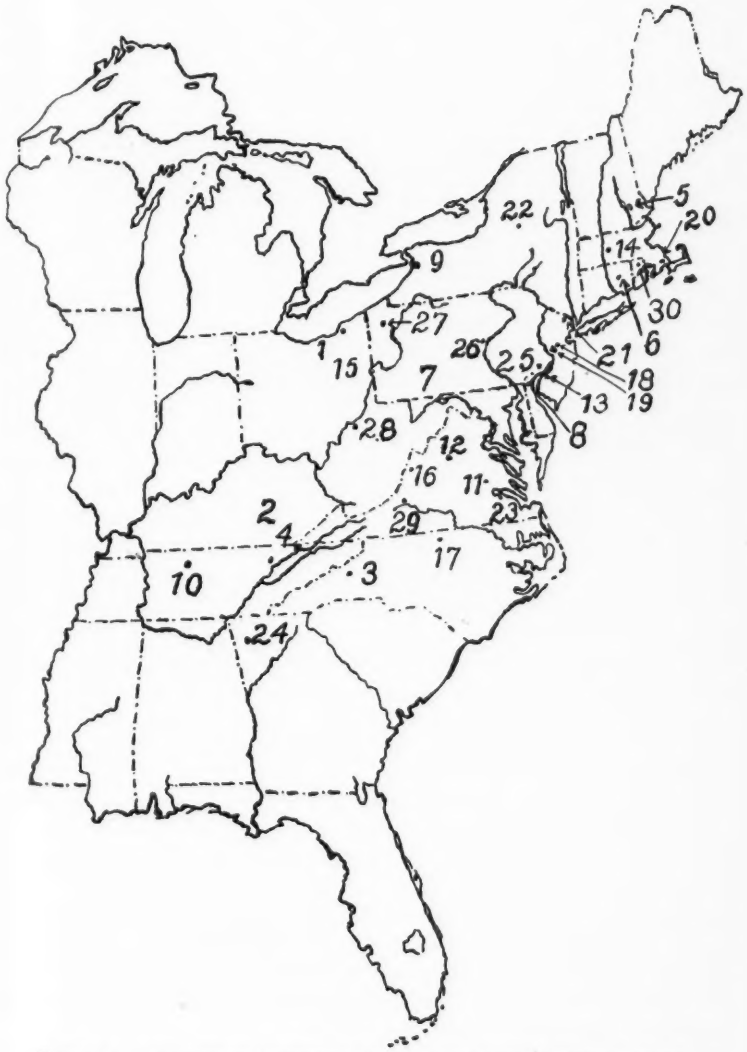
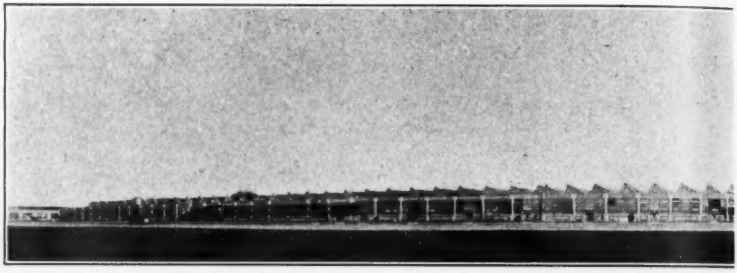


FIGURE 1.—LOCATION OF SYNTHETIC FIBER PLANTS IN THE UNITED STATES



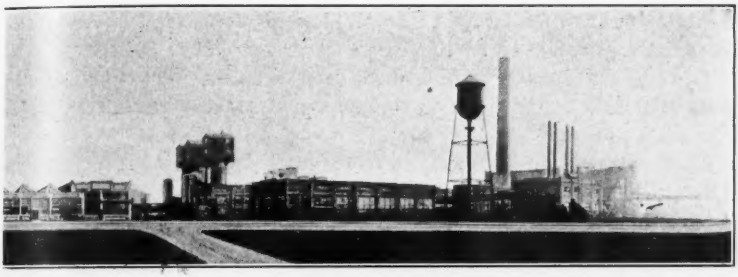
TEXTILE AREA, TUBIZE CHATILLON

tons of caustic soda and 33,000 tons of carbon disulfide were used by this industry in our own country. Of the amount of cellulose consumed, about 63,000 tons were sulfite wood pulp while about 33,000 tons of cotton linters were used. Approximately 11,000 tons of acetic anhydride and about the same amount of acetic acid were consumed. This should give a little idea of the magnitude of the industry.

Future Possibilities

Much has been said already about research and its value to industry. It is a subject which will stand an immense amount of consideration. Before considering some of the more recent and the near-future developments which have resulted and will result from research work in this industry, it would be well to think over what has been accomplished in the past. The industry did not develop by the research work of one man but by the earnest endeavors of countless workers. This brings to mind the incident told of a very prominent banker, during an interview with an eminent rayon expert, who was inquiring about the competitive effect of rayon on natural silk. He wished to invest a large sum of money but wanted to be reassured as to the future of the synthetic fiber industry. He asked the expert all sorts of questions about the relative merits of the two fibers. He also wished to know something about the efficiency of production of natural silk and if the quality could not be improved so that it would still hold its position in advance of the improvements in rayon. The expert finally remarked that "while the silkworm is a wonderful little factory, the only trouble with him is that he has not improved on his product in the last ten thousand years while in the artificial silk game men are working night and day to improve their product."

In Chardonnet's first commercial plant the spinning took place by the "wet" method. The thread from the spinneret passed down one side of a U-tube full of water and up the other side to the bobbin. The water was considered necessary to "set" the filaments. These tubes being of glass



CORPORATION, HOPEWELL, VIRGINIA

were naturally subject to breakage. It happened that an operator continued to spin after the tube had broken. Chardonnet noticed the filaments were being coagulated and was surprised and highly gratified to find that the thread was stronger and more lustrous than before. This led to the dry spinning method.

We have mentioned the fact that rayon is made from cellulose while natural silk is composed of protein material. The two differ widely in chemical composition as well as in some of their most important properties. While the idea at first was the production of an artificial silk, it was soon discovered that what had been developed was really an entirely new synthetic fiber which occupies a distinct place today among the basic textile fibers. This synthetic fiber absorbs moisture very readily, which would not be so disturbing were it not for the fact that wet rayon is very tender and loses about one-half its dry strength. Much has been done to improve the product and an immense amount of investigation is being carried on to increase the strength, especially when wet.

That considerable advance has been made along the line of increased strength is shown by the appearance on the market of rayon sewing silk which compares very favorably with natural sewing silk. If an unripe viscose sirup is spun into a bath of concentrated sulfuric acid, a thread is produced which has a much higher tensile strength than the ordinary thread.

Lilienfeld is very active in rayon research fields. He holds patents covering the introduction of nitrogen into the viscose. The resulting thread is stronger and is a closer approach to natural silk chemically than any other synthetic fiber. By treating viscose with a fatty acid and a derivative of ammonia he is able to produce these xanthacetic acid compounds.

Besides the above fields, he, with others, is investigating the possibilities of producing synthetic fibers and films from cellulose ethers. Work is being conducted along the line of mixed esters of cellulose. For instance, it has been found that films made from the nitroacetates of cellulose are much less

inflammable than the straight nitrocellulose films and also have a greater tensile strength than either the nitrate or acetate films.

Threads and films have been made from cellulose formate. This presents excellent possibilities if the brittleness of the resulting thread can be overcome.

Another process which is in the experimental stage proposes to produce a cellulose butyrate thread. The LaFrance-Kohorn Company plans to manufacture this type of silk.

There are countless problems connected with the present commercial methods for producing rayon which are waiting for research workers to solve. In addition to this we must keep in mind the necessity for an increase in the knowledge of our chief raw material. This information can come only from scientific investigations on cellulose itself. Why is it that we are not using wood pulp in the nitrate and acetate processes? Why is it necessary to have spruce sulfite wood pulp? Truly this industry presents a wonderful field for the hard-working chemist or chemical engineer.

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UNITED STATES CIVIL-SERVICE EXAMINATION FOR METALLURGIST

The United States Civil-Service Commission announces an open competitive examination for METALLURGIST at an entrance salary of $3800 a year. Applications for the examination must be on file with the U. S. Civil-Service Commission at Washington, D. C., not later than October 29, 1930. This examination is to fill vacancies in the Departmental Service, Washington, D. C., and in the Federal classified service throughout the United States.

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STUDIES ON THE MECHANISM OF AMMONIA SYNTHESIS OVER IRON CATALYSTS*

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The story of the early laboratory experiments of Haber, Nernst, and others on the catalytic production of synthetic ammonia has been told many times. It is not surprising that such should be the case, for this work, together with its development into the first Haber-Bosch commercial synthetic ammonia unit in 1913, seems destined to be recorded in history as one of the most brilliant accomplishments of modern chemical and engineering research.

In the present paper, however, the synthesis of ammonia will be considered from a different point of view. No attempt will be made either to recount the history of that brilliant period in the synthetic ammonia industry or to describe any of the similar interesting industrial developments that have since occurred in various countries of the world. Instead, a brief resumé will be given of the results of experiments that have been performed in an endeavor to elucidate the mechanism of ammonia synthesis over iron catalysts, and to find out why various synthetic ammonia catalysts behave as they do under specified conditions of temperature, gas pressure, and gas purity.

It will first be necessary to discuss briefly the general types of synthetic ammonia catalysts that have been most studied and the difference in composition between the very active and the relatively inactive synthetic ammonia catalysts with which we shall be concerned. Pure iron catalysts are known not to be very effective for the synthesis of ammonia. If, however, the iron catalyst contains a small percentage of any one of several oxides, such as, for example, Al_2O_3, ZrO_2, or SiO_2, its activity is very materially enhanced. These small percentages of added activators are commonly known as "promoters." Such catalysts shall be referred to throughout the present paper as singly promoted catalysts. Larson and his coworkers at the Fixed Nitrogen Research Laboratory in Washington have developed an iron catalyst containing both a small percentage of an alkaline oxide such as K_2O (usually about 1%) and a small percentage (1 to 3% ordinarily) of an acidic oxide such as Al_2O_3, SiO_2, or ZrO_2 (*1*), (*2*), and (*3*). The activity of such a doubly promoted catalyst operating on pure 3:1 hydrogen-nitrogen gas at 100 atmospheres pressure and at a temperature of 450° is 50% or so greater than that of a singly promoted catalyst.

The synthetic ammonia catalysts described in the present paper, as well as the most of those used commercially, have been made by adding appropriate combinations of promoter materials to fused Fe_3O_4, cooling the

* This paper is essentially that given at the symposium on "Industrial High-Pressure Reactions" held by the Division of Industrial and Engineering Chemistry at the Cincinnati meeting of the American Chemical Society, September 8–12, 1930.

resulting mixture, crushing the promoted Fe_3O_4 to appropriate size and then reducing the oxide granules with hydrogen or 3:1 hydrogen-nitrogen gas.

The relative activities (*2*) of these various types of synthetic ammonia catalysts operating at 5000 space velocity* on pure 3:1 hydrogen-nitrogen gas at 450°C. and a pressure of 100 atmospheres is summarized in Table I below:

TABLE I

Activity of Certain Promoted Catalysts and Composition of Oxides before Reduction

No.	*Total iron, per cent*	*Free iron, per cent*	*Ferrous iron, per cent*	$\frac{\text{Ferrous}}{\text{Ferric}}$	Al_2O_3	K_2O	NH_3 *at 450°C. and 30 atmos., per cent*	*5000 S. V. 100 atmos., per cent*
918	72.84	2.37	25.03	0.551	..	..	3.30	5.49
920	72.58	1.23	25.35	0.551	..	0.20	1.57	3.43
921	71.99	1.00	26.16	0.573	1.31	..	5.35	9.35
922	71.99	0.89	24.55	0.527	1.05	0.26	5.80	13.85

It is particularly interesting to note that whereas the addition of K_2O to a pure iron catalyst decreases its activity, its addition to a catalyst already promoted with Al_2O_3 produces a catalyst having an activity on pure gas very much superior to that of the catalyst promoted with Al_2O_3 alone. Properly promoted catalysts, when operated on pure 3:1 gas at temperatures of 450 to 550°C. retain their activity toward ammonia synthesis for an almost indefinite period of time. This remarkable characteristic makes them especially valuable for various mechanism studies in which a constant and reproducible activity is especially desired.

Many methods of attack have been utilized in recent years for obtaining information on the mechanism of catalytic reactions. These for the most part may be grouped into the experiments on (1) adsorption of the various gaseous constituents on catalysts; (2) kinetics of gas reactions over catalytic materials, both as regards the dependence of the rate of reaction upon the gas composition and pressure, and its dependence upon the temperature of the catalysts; (3) the poisoning of catalytic materials by various amounts of such poisons; and (4) the nature of the solid phase used as a catalyst, particularly as regards its possibility of undergoing reaction with any of the gaseous constituents with which it may be brought in contact, and also as regards its crystal size and physical characteristics. There are in addition certain miscellaneous types of experiments that do not fall very well under any of the above-mentioned modes of study but give valuable information as to the possible cause of the catalytic activity of certain materials. The work on synthetic ammonia catalysts shall now be reviewed from the standpoint of the various types of mechanism studies,

* Space velocity is defined as the number of liters of gas flowing (measured at 0°C., and 1 atm. pressure) per liter of catalyst per hour.

and a final summary given as to the present status of the theory of the catalytic synthesis of ammonia.*

Adsorption of Hydrogen, Nitrogen, and Ammonia on Iron Catalysts

Very little information has been published on the adsorption of hydrogen, nitrogen, or ammonia on the synthetic ammonia catalyst. Indeed, by the time the mechanism studies on ammonia catalysts were started it had already been generally conceded that the activity of a catalytic material would in all probability not be proportional to the total amount of the various reacting constituents adsorbed (*4*). It seemed rather that only a comparatively small portion of most catalytic surface is active. Consequently it is not the total extent of surface but the relative numbers of these "active points or centers" that will determine the activity of catalytic materials (*5*). Accordingly, no extended researches on adsorption of hydrogen, nitrogen, and ammonia on iron ammonia catalysts have been made. Such results as have been obtained at this laboratory,** however, would lead to the following conclusions:

(1) Small but definite quantities of both hydrogen and nitrogen are adsorbed by synthetic ammonia catalysts at 450°C. and lower. The activity of variously promoted catalysts is not proportional to the amounts of either of these gases adsorbed or to the ratios of the two adsorbed.

(2) The adsorption of ammonia at temperatures below that at which appreciable reaction of ammonia with the iron to form nitride can occur is not proportional to the activity of the various iron ammonia catalysts.

One very important and significant type of experimental work has been carried out by Kistiakowsky (*6*) on synthetic ammonia catalysts in an effort to learn more of the nature of the nitrogen adsorbed on an active catalyst—whether for example it is present as molecules or atoms. His experiment consisted in bombarding with electrons a synthetic ammonia catalyst in an atmosphere of nitrogen at low pressure and noting the accelerating potential that had to be applied to the bombarding electrons to give them sufficient velocity to produce upon collision ionization of the nitrogen gas adsorbed upon the surface of the catalyst. It was found that whereas the minimum potential drop through which an electron must fall to produce ionization of a molecule of nitrogen with which it collides in the gas phase (not on the catalyst) is about 17 volts, ionization of the nitrogen adsorbed on the catalyst could be obtained at 11 volts. Indirect evidence

* A very excellent and detailed summary of the work on the mechanism of ammonia synthesis is given by Frankenburger in Ullmann's "Enzyklopädie der Technischen Chemie," 1928.

** The adsorption values on which these conclusions were made are from some unpublished data at the Fixed Nitrogen Research Laboratory obtained by A. T. Larson and his co-workers.

led him to attribute this 11-volt ionization to nitrogen atoms adsorbed on the catalyst. The 11-volt ionization was also found when nitrogen was adsorbed upon the surface of Ni, Cu, and Pt, though to a markedly smaller extent than on iron. Definite conclusions as to the mechanism of ammonia synthesis are difficult to draw from this work, though it is tempting to suspect that the form of nitrogen responsible for the marked occurrence of the 11-volt ionization on iron surfaces may be connected with the necessary activation through which nitrogen molecules have to go before combining with hydrogen to form ammonia.

Taylor and Dew (*7*) measured the total adsorption of ammonia on iron, Ni, Cu, and Fe-Mo catalysts. They also obtained the heats of adsorption of ammonia on these various materials. The heat measurements were carried out in such a manner that the heat evolved per unit of gas adsorbed could be obtained for each of the successive amounts of gas adsorbed. In the case of ammonia on Fe the first gas adsorbed evolved heat to the extent of 16,000 calories per mol of ammonia. This value gradually decreased until the last quantities of ammonia that were adsorbed near one atmosphere pressure evolved about 8000 calories per mol of ammonia adsorbed. This maximum initial differential heat of adsorption of ammonia on Fe is greater than for any of the other materials tried, values of 11,300 calories having been obtained on Ni and 8700 calories on Cu. The relationship between this higher heat of adsorption of ammonia on iron as compared to Cu and Ni and the superiority of Fe as a catalyst is not clear.

Kinetics of Ammonia Synthesis

Passing now to the second mode of experimental investigation of catalytic materials, we shall consider the work done on the kinetics of the reaction

$$3H_2 + N_2 = 2NH_3.$$

The per cent ammonia in equilibrium with a 3:1 mixture of hydrogen-nitrogen gas increases with pressure but decreases with a rise in temperature. At 450°C. and 1 atmosphere pressure it is only 0.23%. Accordingly, any kinetic experiments on the rate of synthesis must of necessity be carried out at high pressure to obtain a sufficiently high equilibrium value to make rate measurements practicable. No such measurements employing different ratios of hydrogen to nitrogen have as yet been published. The measurements are rendered extremely difficult if not altogether impossible by the fact that the 13,000 calories of heat evolved per mol of ammonia formed tend to produce temperature inhomogeneities in the catalytic material through which the stream of hydrogen-nitrogen is passing. Kunsman (*8*) has measured the rate of ammonia decomposition on iron catalysts.

As mentioned in a later paper by Kunsman, Lamar, and Deming (*9*), however, interpretation of the results is complicated by the fact that the experiments have been carried out in such a manner that the catalytic surface was at times, doubtless, one of the nitrides of iron formed by the reaction of ammonia with the iron catalysts and at other times metallic iron. In general, the rate of decomposition was proportional to the partial pressure of ammonia but inversely proportional to the partial pressure of hydrogen. It is thus apparent that the existing data on the kinetics of ammonia synthesis and decomposition on iron are not sufficient to warrant interpretation in terms of the mechanism of ammonia synthesis.

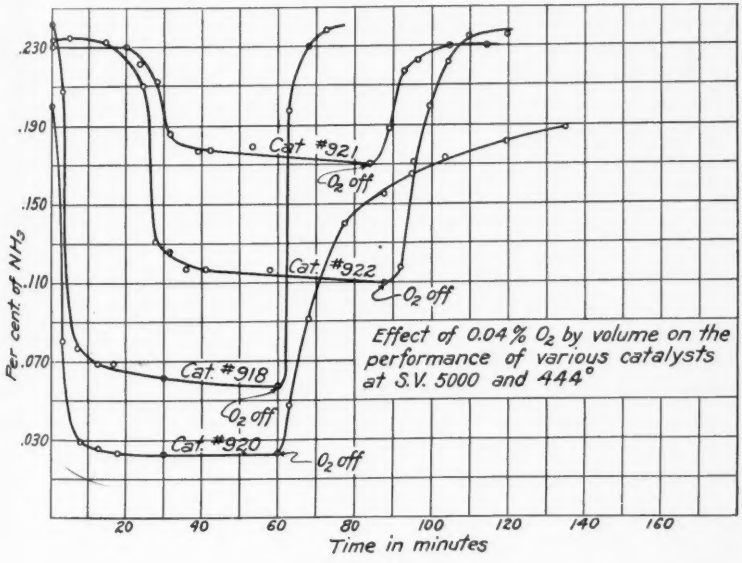

FIGURE 1

Poisoning Experiments

It was early discovered that oxygen, water vapor, and other gaseous oxygen-containing materials, such as CO and CO_2, were poisons for iron synthetic ammonia catalysts. Furthermore, it was known that to some extent at least such poisoning was reversible, *i. e.*, the catalyst would recover much of its activity when poisoned gas was replaced by pure gas. Almquist and Black (*10*), however, were the first to investigate quantitatively the poisoning action of oxygen and water vapor upon synthetic ammonia catalysts.

They passed a 3 : 1 gas mixture at a rate corresponding to 5000 space velocity over a synthetic ammonia catalyst at one atmosphere pressure and 444°C. At some definite time, the pure gas was replaced by a stream of gas poisoned with known amounts of oxygen or water vapor. Simultaneously, analysis of the gas leaving the catalyst for both ammonia and water vapor was begun. Knowing the amount of poison being passed into the catalyst and obtaining by the analysis the amount of poison passing out of the catalyst tube, they could calculate the amount of poison retained by the catalytic material and could in addition ascertain the activity of the catalyst at various times during the poisoning run.

The variation with time of the per cent ammonia in the exit gas during such a poisoning run is shown in Figure 1, taken from the article of Almquist and Black. It will be noted that pure iron catalyst 918 decreased in activity immediately whereas the singly promoted catalyst 921 or doubly promoted catalyst 922 fell off only after the lapse of a definite interval of time. The lag between the time at which poisoned gas was passed over catalyst 921 or 922 and the time at which the decline in activity toward NH_3 synthesis first occurred, was explained as a period during which poison is accumulating on part of the catalyst. Both of the promoted catalysts, however, are sufficiently active to produce the equilibrium per cent ammonia at 450°, 1 atmosphere, and 5000 S.V., even after 75 or 80% of the catalyst is badly poisoned.

TABLE II

Oxygen Retained as Oxide by the Catalyst

Catalyst	O_2 *input, mg./min.*	*Concn. of* O_2 *in gas, vol.*	*Duration of run, min.*	O_2 *input, mg.*	O_2 *in exit, mg.*	O_2 *retained, mg.*
918	0.25	0.04	60	15.0	13.9	1.1
	1.00	0.16	60	60.0	58.4	1.6
920	0.25	0.04	60	15.0	14.5	0.5
	1.00	0.16	60	60.0	58.8	1.2
921	0.125	0.02	107	13.4	8.6	4.8
	0.25	0.04	84	21.0	14.4	6.6
	0.50	0.08	78	39.0	29.6	9.4
	1.00	0.16	76	76.0	63.8	12.2
	1.50	0.24	60	90.0	75.5	14.5
922	0.25	0.04	88	22.0	15.9	6.1
	1.00	0.16	74	74.0	63.3	10.7

The amounts of water vapor retained by each of the catalysts under various conditions are recorded in Table II. The amount retained by any one catalyst is proportional, approximately, to the square root of the partial pressure of water vapor. The pure iron catalyst picked up only about one-tenth the amount of water vapor retained by either the doubly or singly promoted catalysts.

The water retained could be very readily removed by replacing the poisoned gas by pure gas. The ammonia conversions soon returned to approximately their former values.

Almquist concluded that the oxygen retained by the catalyst was actually held in the form of oxide. However, extrapolation from the data of Eastman and Evans (*11*) on the $Fe\text{-}Fe_3O_4\text{-}H_2O\text{-}H_2$ equilibrium indicated that at least 16% water vapor would have to be present in the gas mixture to convert the iron to Fe_3O_4. It was, therefore, postulated by Almquist (*12*) that the oxide formed by the 0.04 to 0.48% water vapor was the result of reaction of water vapor with surface iron atoms having greater thermodynamic activity or free energy content than the iron atoms in the normal lattice. Calculations in fact showed that the excess free energy possessed by these surface atoms over and above that possessed by ordinary iron was approximately 13,000 calories per gram atom of iron. Furthermore, these active surface atoms presumably were closely associated somehow with the synthesis of ammonia, inasmuch as the per cent ammonia produced by the poisoned catalyst seemed inversely proportional to the oxide retained.

On the basis of the poisoning experiments it was found possible to calculate the ratio of the total iron atoms in a catalyst sample to those picking up oxygen from these small percentages of water vapor (assuming that no more than one oxygen atom is retained by one iron atom). The results of such calculations are shown in Table III. It will be noted that when sufficient poison is added to decrease the activity in each case to about 0.06% NH_3, the good catalyst has approximately one iron atom out of every two hundred covered with oxygen poison, whereas the pure iron sample has but one in every two thousand so covered. This would indicate that the active surface of the good catalysts is of the order of 10 times that of the pure iron catalysts.

TABLE III

Ratio of Active Iron Atoms to Total Number Present

Catalyst	O_2 *in gas,* %	*Final* NH_3, %	*Mg. of* O_2 *reld.*	*G. atom of* O	*Ratio total atoms* Fe *to active* Fe
918—pure iron	0.04	0.06	1.1	0.000069	2440
918—pure iron	0.16	0.03	1.6	0.0001	1680
921—iron + Al_2O_3	0.04	0.17	6.6	0.00041	404
921—iron + Al_2O_3	0.08	0.12	9.4	0.00058	280
921—iron + Al_2O_3	0.16	0.09	12.2	0.00076	218
921—iron + Al_2O_3	0.24	0.06	14.5	0.00091	183

The experiments of Almquist and Black have recently been extended to high pressures by Emmett and Brunauer (*13*). The high pressure results give even more definite proof that the oxygen is being retained as oxide and not as adsorbed water. The amount of oxide retained by a particular catalyst was found to be proportional to $\sqrt{P_{H_2O}/P_{H_2}}$. Thus at 100 atmos-

pheres pressure 0.32% water vapor in 3:1 hydrogen-nitrogen gas resulted in the deposition of the same amount of oxide as 0.32% water vapor at 1 atmosphere pressure. Again good promoted catalysts retained some 10 to 20 times the amount of oxide retained by pure iron catalysts. Typical curves showing the variation of per cent NH_3 with time after the turning on of the poisoned gas are shown in Figure 2. The ammonia percentage quickly drops to a steady value. Measurements showed that after the ammonia percentage reached a steady value no further measurable amount of oxygen was picked up by the catalytic material. When pure gas was substituted for poisoned gas the catalysts recovered quickly to the former activity. The high pressure results are, accordingly, also consistent with the conclusion of Almquist that the atoms active in the synthesis of ammonia are the ones poisoned by small percentages of water vapor.

Study of the Physical and Chemical Characteristics of Promoted and Pure Iron Catalysts

In an effort to explain the action of the promoters that are commonly added to the Fe_3O_4 from which by reduction ammonia catalysts are obtained, Wyckoff and Crittenden (*14*) subjected a number of promoted catalysts and pure iron catalysts to a crystal structure study by the use of X-rays. Several interesting facts were revealed. Powder photographs of unreduced Fe_3O_4 samples containing a little excess dissolved iron, showed the presence of FeO as a separate phase in the solid oxide. When, however, an amount of Al_2O_3 equivalent to the known excess of FeO was added to the molten Fe_3O_4 in preparation, not only did the FeO lines fail to appear on the X-ray powder photographs, but no lines characteristic of Al_2O_3 appeared even though the latter material was added in sufficient quantities to make it probable that it would have appeared had it been present as separate phase. It was concluded that the FeO and Al_2O_3 reacted to form $FeAl_2O_4$. This substance apparently dissolves in the Fe_3O_4 forming a solid solution in which the aluminum atoms merely replace some iron atoms in the normal Fe_3O_4 lattice.

One other interesting fact was brought to light by the X-ray examination. Photographs taken of samples of pure iron obtained by the reduction of pure Fe_3O_4 were found to be identical with those obtained from iron catalysts containing Al_2O_3 and K_2O as promoters and obtained by the reduction of Fe_3O_4 to which Al_2O_3 and KNO_3 had been added. The X-ray diffraction patterns on the powder photographs were indicative of no extra large crystals in either sample. When, however, these same samples were again examined by powder photographs after each had been heated to 600°C. for four hours, it was found that the pure iron catalysts gave a powder photograph definitely indicative of crystal growth, whereas the promoted iron catalyst still showed the normal small crystal pattern.

It was thus definitely established that one function of the promoter in synthetic ammonia catalysts was to exercise a sort of "guard action" tending to prevent the growth of the iron crystals. The retarding of such crystal growth necessarily resulted in the preservation of a larger surface per unit weight of catalyst.

Both this experiment and that of Almquist and Black demonstrated the existence of a greater active surface per unit weight of promoted catalyst than of pure iron catalyst. It cannot be concluded, however, from either

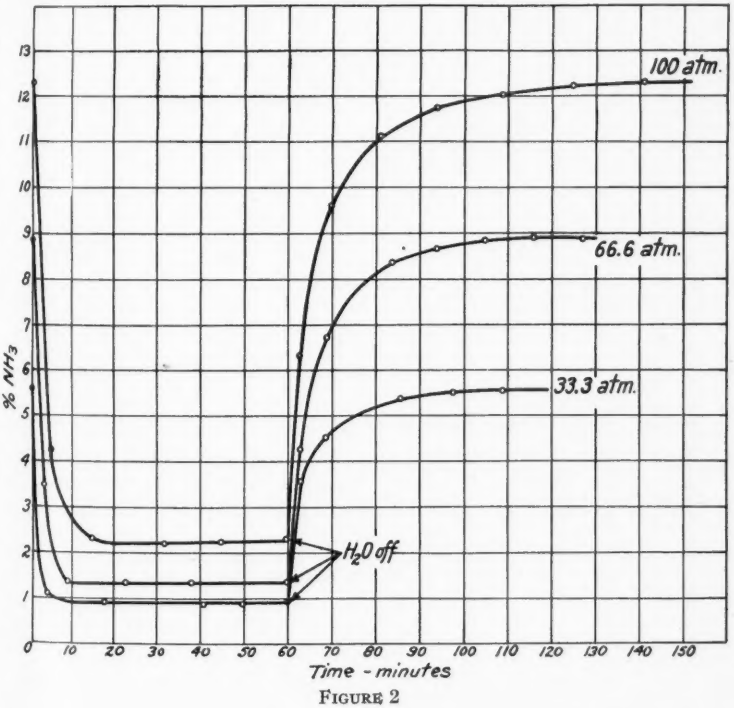

FIGURE 2

of these experiments that the activity per unit area of catalyst surface is any different on the promoted than the pure iron catalyst.

There is, however, one definite indication of a qualitative difference in the nature of the surface dependent upon the type of promoter used. The evidence for this qualitative difference is to be found in the strikingly different ways in which the activities of different catalytic materials vary with pressure. Catalysts of pure iron or those promoted with certain substances decrease very rapidly in activity as the pressure is increased. Other

catalysts possessing the same activity as the first-mentioned ones at low pressures retain a high activity at high pressure. For example, doubly promoted catalysts containing both K_2O and Al_2O_3 promoters are as a rule characterized by retaining their activity at high pressure much better than iron catalysts promoted with Al_2O_3 alone. The different manner in which the efficiency* of a catalyst varies with pressure is well illustrated in a diagram taken from the article of Larson and Dodge (*15*) and shown in Figure 3. All of the catalysts shown are promoted catalysts capable of

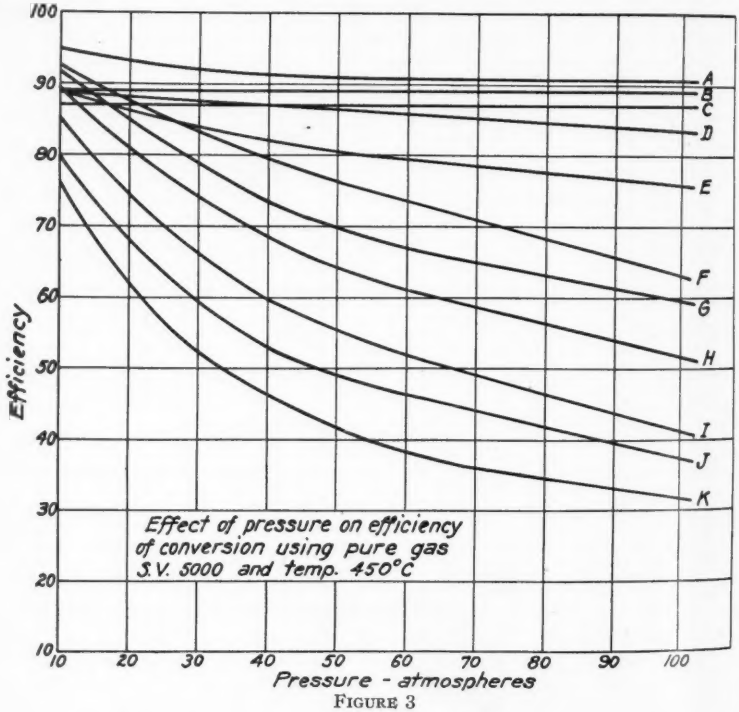

FIGURE 3

retaining their activity on pure gas for long periods of time and differing only in the nature of the promoter materials. This reproducible variation in the behavior of catalysts with pressure seems to constitute definite evidence that the promoting material not only controls the total amount of surface per unit weight of catalyst but also the qualitative nature of that surface.

* By "efficiency" is here meant merely the fraction of the equilibrium value of ammonia existing in the exit gas from a catalyst tube operating at some definite temperature, pressure, and space velocity.

In an attempt to explain the remarkable efficiency of iron catalysts toward the production of synthetic ammonia from hydrogen and nitrogen, a number of workers have investigated the conditions under which nitrides of iron can be formed. The question has arisen as to whether catalytic ammonia synthesis might not take place as a result of nitrogen reacting with iron to form some sort of iron nitride which would then be reduced by hydrogen to form ammonia and restore the metallic iron. Baur and Voerman (*16*), Maxted (*17*), and others tried without success to form iron nitride by the direct action of nitrogen at pressures as high as 200 atmospheres on iron between the temperatures of 400° and 700°C. They concluded that the dissociation pressures of iron nitrides were greater than 200 atmospheres over the temperature range investigated. Noyes and Smith (*18*) have shown the possibility of measuring the dissociation pressure of the nitrides of iron by an indirect method. If one adds, in the usual manner, the equation

$$2NH_3 = 3H_2 + N_2 \qquad K_1 = \frac{(P_{H_2})^3(P_{N_2})}{(P_{NH_3})^2} \qquad (1)$$

and the equation

$$2Fe_xN + 3H_2 = 2xFe + 2NH_3 \qquad K_2 = \frac{(P_{NH_3})^2}{(P_{H_2})^3} \qquad (2)$$

he obtains the equation

$$2Fe_xN = 2xFe + N_2 \qquad K_3 = K_1K_2 = P_{N_2} \qquad (3)$$

Accordingly, by combining the equilibrium constants for reactions (1) and (2), one can obtain a value for the equilibrium constant of reaction (3) which when expressed in atmospheres gives the dissociation pressure of the particular nitride involved. Noyes and Smith measured the equilibrium for reaction (2), combined the value with the well-known equilibrium constant of reaction (1), and thereby obtained for the first time an approximate value for the dissociation pressure of the nitrides of iron formed by the passage of ammonia over iron. It was concluded that the nitride of lowest nitrogen content formed on passing ammonia over iron possessed a dissociation pressure of about 20,000 atmospheres at 460°C. Accordingly, at the pressures ordinarily used in producing synthetic ammonia it would not be possible for ordinary metallic iron to react with N_2 to form a stable nitride which could then react with hydrogen to form ammonia and iron.

Frankenburger (*19*) has calculated, however, that the iron atoms shown by Almquist to be capable of reacting in the presence of 0.04% water vapor, in contrast to the 16% required to oxidize ordinary iron to Fe_3O_4, would likewise be capable of reacting with nitrogen at a pressure of one or two atmospheres* rather than at 20,000 atmospheres only. The alternate

* For critical discussion of this calculation, see reference (*13*).

formation and reduction of such a surface nitride might, he concludes, constitute the mechanism through which the catalytic synthesis of ammonia over iron occurs.

Recently, a phase rule study of the Fe-N_2 system (*20*) has shown that Fe_4N, the iron nitride of lowest nitrogen content made by passing ammonia over iron, has a dissociation pressure of only 5300 atmospheres at 460° instead of 20,000 atmospheres. This lower value would permit an even larger fraction of the surface iron atoms to form some sort of surface nitride than would be possible were the dissociation pressure 20,000 atmospheres.

In a recent series of experiments, Frankenburger and Mayrhofer (*21*) have endeavored to find whether or not hydrogen, as well as nitrogen, is capable of combining with very unsaturated atoms such as are found upon catalytic surfaces. Their experiments consisted in brief of vaporizing iron from a filament in a low-pressure atmosphere of hydrogen onto a glass wall cooled in liquid air to −190°C. They found that by regulating the amount of moisture in the hydrogen the atomic ratio of iron to hydrogen in the material deposited on the wall could be reduced to 1:1. They interpreted their results as indicating that the iron atoms deposited on an ice film at −190° were kept separated by the ice particles into very small groups of not more than four or five atoms each. This might be considered equivalent to obtaining a surface of atoms similar to the "active iron atoms" that are believed responsible for the activity toward ammonia synthesis. Each of these iron atoms was capable of holding a hydrogen molecule in some sort of a Fe-H_2 linkage. It is quite possible that this work may be indicative of the tendency of active surface iron atoms to react with hydrogen, forming, momentarily at least, some active combination essential to rapid reaction with nitrogen to form ammonia. Attempts by these workers to form Fe-N_2 compounds by a similar technic have so far given entirely negative results.

At the present time, then, one can summarize all of the various experimental work that has been carried out on synthetic ammonia by postulating a mechanism of ammonia synthesis consisting in the reaction of nitrogen molecules with highly active surface iron atoms forming some sort of surface nitride which when brought into contact either with gaseous hydrogen molecules or possibly with hydrogen molecules adsorbed or momentarily combined with adjacent active iron atoms will result in the formation of a surface NH or NH_2 group intermediate to the completion of the ammonia molecule. Promoters added to iron synthetic ammonia catalysts presumably function in a two-fold manner, both to maintain a large catalyst surface by preventing the growth of iron crystals in the catalyst and also to affect in some way the qualitative nature of the surface immediately surrounding the promoter molecules.

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A SIMPLE SUBSTITUTE FOR A KIPP GENERATOR

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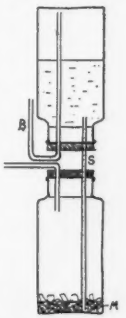
It frequently happens that individual gas generators for elementary students are desired. The supply of Kipp generators is usually inadequate. The accompanying diagram illustrates a simple substitute which can be quickly made from the equipment usually present in the elementary locker. Ordinary gas bottles and 4- to 5-mm. tubing serve best. It is a convenient source of hydrogen sulfide for studying the insoluble sulfides. Since it is automatic, it works very well as a source of carbon dioxide in the preparation of sodium bicarbonate by a modified Solvay process.



The breather tube *B* may be led to a sink or waste beaker instead of being left free. The mat *M* of glass or copper wool is essential to the smooth operation in order to keep the reacting material (marble or iron sulfide) above the lowest level of the acid. The tube *S* may be varied in length to deliver gas at different pressures.

The actual preparation of the gas and the construction of such an apparatus is far more instructive than using tanks of compressed gas.

THE METHODOLOGY OF SCIENTIFIC RESEARCH*

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It is difficult at first glance to account for the varying success of the men of apparently equal endowments and training who have devoted themselves to scientific research. Consequently, it seems worthwhile to seek out the reasons underlying the success of those men of genius who have become eminent in science.

First and foremost is the *gift of observation*, that is to say, the faculty of fixing one's attention on facts which appear unexpectedly. Some workers notice everything which occurs during their experiments, while others observe nothing. Lord Rayleigh noted the discordance in the density of nitrogen derived from the air and that prepared chemically, and was thus led to the discovery of the rare gases of the atmosphere. Other scientists had been confronted with this discrepancy but had given it no attention. Lavoisier placed iron filings in water and noticed the continuous liberation of a small number of minute bubbles, an observation that resulted in the discovery of the composition of water. Auer von Welsbach while calcining precipitated thoria was struck by the exceptional glow emitted, the Welsbach mantle resulted; others had seen the same thing but it had not arrested their attention.

This faculty of keen observation is partly a natural gift that is usually inherent in those of impressionable temperaments, but it may also be developed by proper methods of education. Chemical manipulations involving the actual handling of materials are of great value here. For example, a stolid pupil may be told to heat a small quantity of iodine in a test tube and to describe all that he has seen. He ought to have seen the violet vapor, the black sublimate, the deposit of small crystals on the colder parts of the tube, and so on, but how many of these details will he actually have noted? A group of children may be sent to a given point in the country with instructions to observe their surroundings. On their return one will have seen only the hills, another, a ditch by the road side, a third, a church steeple.

A second quality essential in scientific research is the *association of ideas*, that is, the ability to bring together at a desired time the enormous number of facts which have accumulated in the memory but which it is very difficult to recall at the opportune moment. It is sometimes said that a document that has been filed and classified is likely to remain buried until the end of time. The same is partly true of the memory from which at the desired moment only a small fraction of the material stored there may be recovered. Men differ greatly in this respect.

The writer remembers with great interest a conversation he overheard between Berthelot and one of his assistants. The latter had been ordered

* Translated by Ralph E. Oesper, University of Cincinnati, Cincinnati, Ohio.

to analyze an antique bronze and Berthelot was inquiring as to his findings. The assistant reported that the bronze contained 6% of tin, and Berthelot asked how he had identified the tin. "After treating the sample with nitric acid the addition of sulfuric acid produced a white, insoluble precipitate." Berthelot said, "Do you not know that lead sulfate is likewise white and insoluble?" "Yes, but I did not think of that." "Have you tried the action of ammonium sulfide on your precipitate to be sure that it will not turn black?" "I did not think of that." "Don't you know that most antique bronzes do not contain tin, but rather lead; haven't you already analyzed several samples of these?" "Yes, but I was no longer thinking about those." In this instance Berthelot and his assistant had exactly the same knowledge available in their memories. In ten seconds, Berthelot recalled the facts and used them, while the assistant, after eight hours of work on this same problem, recalled nothing pertinent to the analysis.

Another example. Long before Lavoisier it was known that metals increase in weight when calcined in the air. Pascal's experiments with the barometer had shown that air has weight. However, no one dreamed there was any connection between these two facts until Lavoisier did so and thus laid the foundations of modern chemistry. Likewise, the impossibility of perpetual motion was recognized long before Sadi Carnot, as was the possibility of converting heat into work. It remained for him to unite these two ideas and so create the science of energy.

This ability is not an innate quality, for children do not possess it, and its acquisition is one of the essential aims of education. Accurate Latin translation, the writing of orations, and the solution of geometrical problems are typical of the subjects best calculated to develop the faculty of using knowledge previously acquired.

A final aptitude, not usually considered in relation to scientific research, although of prime importance, is *common sense:* that is, that faculty which Pascal termed the "*sense of finesse*" (intuition) as opposed to the "*sense of geometry*" (strict logic). It is but seldom that one can give his exact reasons for a certain line of conduct. Sometimes one's knowledge of the primordial facts is insufficient to construct a line of reasoning, but more often one is confronted by different points of view which lack common factors and which consequently cannot be treated by the customary methods of reasoning.

First of all, common sense plays an important rôle in the choice of a life work. To become a great scientist it is not sufficient to have been a good experimenter. It is essential that the field of endeavor be of importance, either from the point of view of advancing theory, or of developing public wealth or the general welfare of mankind. Examples of the first class are Fresnel's study of the theory of light, Sadi Carnot's investigations of the

motive power of heat, Berthelot's researches on organic synthesis, and St. Claire Deville's work on dissociation. Instances of the more immediately practical are the work of Gay-Lussac on the manufacture of sulfuric acid, the liquefaction of air and the synthesis of ammonia by Claude, incandescent gas lighting by Auer, improvements in the candle industry by Chevreul, chlorine bleaches by Bertholet, the electric furnace by Moissan. Obviously there is need of workers to study and cultivate all the narrow corners of science, but they cannot hope to achieve the same fame as those who open new realms into which they are followed by numerous workers content to do the conventional routine tasks. Those scientists who are wise enough to recognize what Taine, in the field of art, called the "dominant characteristics" are almost certain to produce work of superior importance.

Common sense plays a second very important part in the choice of the hypotheses which serve as a starting point for the majority of scientific researches. It is often stated that a man may make whatever hypotheses he pleases, that these may even be absurd and yet yield interesting conclusions, provided that he follow meticulously the rule of Claude Bernard: "Subject every experiment to rigid control and abandon a hypothesis ruthlessly as soon as a single definitely established fact does not conform to it." But it is certainly true that a judicious selection of hypotheses will lead more rapidly to useful results with economy of labor and with increased efficiency.

When St. Claire Deville, having found that the temperature of the oxy-hydrogen flame was much lower than expected, postulated that the combination of hydrogen and oxygen was not complete, his choice of possible explanation was a wise one and its verification resulted in the very important discovery of the phenomenon of dissociation. Pasteur made an equally judicious choice when he presupposed that no living thing could develop spontaneously. He might have assumed the contrary to be true and yet have reached the same conclusions after having learned from experiments that his supposition was incorrect. This, however, would have involved much more labor before a definite conclusion could have been reached. It was a long time before his adversaries, who maintained the opposite view, admitted the facts.

A third rôle of common sense is involved in the interpretation of experimental findings. Great difficulty arises from the errors which all measurements inevitably include. Instead of recognizing this fact, experimenters sometimes allow themselves to be drawn into absurd conclusions by regarding experimental errors as new properties of matter. Classic examples may be cited. Schutzenberger announced that atomic weights are not constant, basing this conclusion on analyses of benzene which did not agree with each other. He was not aware that carbon dioxide had passed through

the walls of the excessively long rubber tubes of his apparatus. Sir William Ramsay believed that he had transmuted silicon into carbon, and copper into lithium, but later realized that the carbon actually came from the grease on his stopcocks, and the lithium from the glass of his apparatus. Hinrichs thought he had proved that the atomic weights of all the elements are whole numbers, a conclusion arising from the erroneous use of algebraic functions. Carvallo deduced from Becquerel's work on the dichroism of crystals that Fresnel's theory of light was inexact. In reality, this disagreement did not reside in the experimental facts but in the algebraic form of an empirical interpolation formula incompatible with Fresnel's theory. Numerous other empirical formulas which represented equally well the experimental results of Becquerel all agreed with this theory of light. Recently, Ernst Cohen has questioned the findings of Mondain Monval on the variation of the solubility of ammonium nitrate at its transformation point and has stated that these are not in agreement with his own figures. As a matter of fact, the disagreement arises only from the arbitrary choice of interpolation formulas. Cohen evidently neglected to take into consideration the fact that curves which would represent equally well the experimental points might have tangents of different slopes, especially in the portions extrapolated beyond the experimental region, as really was the case.

On similar grounds, a great many of the pronouncements of modern physics ought to be closely scrutinized, especially those which deal with radioactivity, isotopes, the velocity of light, the distribution of colloids at various levels, and so on. The urge to find new facts and especially those that apparently contradict the accepted data seems, in many instances, to have paralyzed the critical sense of those who write on these topics.

Common sense also plays a very useful rôle in the establishment of scientific theories and in the coinage of the new terminology necessitated by them. Only too often is it necessary to guard against the useless complications and obscure terms that needlessly burden science today. For example, the expression "false equilibrium" is quite current though it is thoroughly contrary to good usage. A chemical system is either in equilibrium or it is not; false equilibria do not exist. The origin of this bizarre expression is due to Duhem. While a student at the École Normale he gave a short account of the important work of J. W. Gibbs on the equilibria of heterogeneous systems, which, however, he did not understand very well. In translating the passage dealing with passive resistance or chemical inertia, he considered the absence of reaction as a necessary and sufficient characteristic of equilibrium. In reality, the state of equilibrium is defined by the double condition that the system does not change spontaneously and that this transformation toward either side may be brought about by an infinitely small expenditure of energy. His error

was pointed out to him, but instead of frankly admitting that he was wrong, he tried to gloss over his mistake by inventing the new term, "false equilibrium," for such systems as are not in equilibrium and which, however, persist unchanged by reason of chemical inertia.

Another example. All the statements of chemical mechanics applied to systems of solutions are based today on considerations involving osmotic pressures. This tradition is solely justified by respect for the authority of van't Hoff; the small pamphlet of Pascal on the authority of factual knowledge of science seems to have been thoroughly forgotten. The very existence of osmotic pressure is debatable, and it is impossible to measure these pressures accurately. They can only be used if they are related to the vapor tensions of solutions by means of a very simple formula due to van't Hoff himself. Innumerable and very exact measurements of vapor tensions are available, and precisely the same lines of reasoning may be followed employing these tensions as are used with osmotic pressures. Consequently there is no valid reason for not adopting this method. However, the expression "osmotic pressure" is so thoroughly rooted that many chemists would find it difficult to follow a discussion in which vapor pressures had been substituted for osmotic pressures. It was the same when Lavoisier demonstrated the non-existence of phlogiston. The chemists of his time did not question the accuracy of his experiments, but they declared that they could not understand a chemistry in which the word phlogiston did not occur because it was the medium in which they were accustomed to think.

Likewise, all the actual theory involving pH will perhaps profit, if the concentration of that fictitious entity known as "hydrogen ion" is replaced by the product of two concrete values: the concentration and the strength of the acid, the latter being measured by the equilibrium constant of the acid against a given standard salt. Very probably, the future will see marked changes in the theories as to the electrolytic composition of solutions, while the concentration and the strength of an acid are immutable magnitudes.

Common sense is a most rare mental quality and is most difficult to acquire. Its development is one of the most important objectives of those studies known as the classical humanities. A curriculum involving nothing but science is very likely to warp the judgment by blinding the pupil to the fallacy of pure logic; literary studies in general are much better in this regard because the diversity of moral and social phenomena which they present tend to familarize the mind with the complexity of the possible points of view. Almost all eminent scientists received an education which was predominantly literary. This was the case with Pascal, Descartes, Huyghens, Lavoisier, the Carnots (father and son), Ampére, Claude Bernard, Berthelot, etc.

In conclusion, the writer wishes to stress the fact that the proper way to train scientists is not to overload the memory of students daily with information, in the belief that to develop a taste for science it is necessary above all to endow their intellectual faculties with a certain orientation and a certain diligence. This is an opinion formulated by the Greeks, for Plutarch said long ago, "The child's mind is not a vessel to be filled, but a fire to be kindled." Recently the American efficiency engineer, F. W. Taylor, repeated this same thought in a slightly different form: "The child's mind should not be considered a sponge that one is content merely to saturate indiscriminately and uselessly for the sole purpose of accumulating information."

New Drugs by Thousands Await Discovery. Never in the history of the world have the possibilities of adding to the list of valuable drugs been so great as at the present time, Dr. Reid Hunt, president of the United States Pharmacopeia Convention and professor of pharmacology at Harvard Medical School, declared at the opening session of the convention's recent decennial meeting in Washington. We may yet get more drugs from the plant and animal kingdoms. There is no limit to the number that the chemist and the pharmacologist may synthesize in their laboratories. But even more important is the possibility that new and important uses may be found for drugs which we already have, Dr. Hunt said.

Some of the saddest pages in the history of mankind have written on them the failure of physicians to see the possibilities for treating disease with well-known chemicals. Ether was known to doctors and chemists for nearly 300 years before it was used as an anesthetic. Another drug, amyl nitrite, a few drops of which relieves the frightful agony of one form of heart disease, was well known to chemists for 23 years before it was used to treat this condition. The same delayed application was repeated in the case of other anesthetics and many other drugs. They were well known chemically for years before any one tried them in the treatment of disease and for the relief of pain. "Today, relief may be obtained anywhere in the world for a few cents, which fifty years ago was beyond the reach of any potentate or Croesus."

Research is needed to investigate the medical possibilities of the 258,000 organic compounds which chemists have already carefully described chemically and physically, Dr. Hunt said. New compounds are being added to the list at the rate of about twenty a day. He declared America's facilities for studying the medical applications of these new compounds are very inadequate compared with research activity in Germany and other European countries.—*Science Service*

Ethyl Gas Approved for Use in Britain. Ethyl gasoline has been given a good bill of health in Britain, provided its handling is attended by ordinary precautions. The questions raised regarding its safety have been investigated by a Departmental Committee on Ethyl Petrol, which has just issued its final report.

The committee worked along lines somewhat similar to those followed in the earlier investigations in the United States, and they took into consideration the results of the American experiments as well. The aspects of the tetra ethyl lead problem on the committee's agenda included danger from lead in street fumes and dust, spillage on the skin, and evaporation and combustion fumes in closed garages. Danger of lead poisoning in the latter case was considered as considerably less than the well-recognized menace of carbon monoxide.—*Science Service*

UNANSWERED QUESTIONS IN THE BIOCHEMISTRY AND GEOCHEMISTRY OF IODINE*

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With the many and extensive studies which have been made on endemic thyroid enlargement, and the definite exhibition of the rôle which iodine plays in the thyroid mechanism, some workers have felt that the problem is solved, so much so that in 1927 McClendon (*1*) closed his excellent review on the subject with the following paragraph:

> Those attacking the problem from the veiwpoint of preventive medicine—physiologists, biochemists, and public health authorities—have accumulated sufficient evidence to justify the assertion that endemic goiter is the easiest known disease to prevent. By further detailed study of the fundamental principles underlying the cause and prevention and with the constant application of scientific data by the state health organizations, we should see the fulfilment of our earlier prediction: Within another generation there will be no endemic goiter problem.

Serious attempts to study this problem from a public health point of view have been made in several directions. Goiter surveys in schools have been made in many localities, and with more or less variant results. Systematic attempts at controlled prophylaxis have been made in a few places. A few investigators have tried to determine the relative amounts of iodine available to human beings in different areas. Biochemists have interested themselves in the composition of the thyroid hormone and its mode of action in regulating metabolism. There are enough uncertainties still remaining to make it worthwhile to discuss briefly some questions which still lack fully satisfactory answers.

I think we may take it as fully settled that the great controlling factor is iodine. Kendall (*2*) succeeded in isolating the active compound in the thyroid gland, and named it thyroxin. Harington (*3*) has shown the chemical structure of thyroxin and confirmed it by synthesis, but the potency of thyroid preparations is not proportional to their iodine content, nor even to the amount of thyroxin that can be extracted from them, so that Kendall (*4*) has suggested that thyroxin is not the completed hormone, but requires some further step in its activation before it becomes effective. The very slow effect of the feeding of thyroid glands, and the fact that thyroxin, even when administered intravenously, does not become active for some hours, lends color to this view. What is the real thyroid hormone, and how does it function in the control of metabolism? To the non-clinical man the administration of dried thyroid or thyroxin to myxedematous persons to increase the metabolic rate, and the administration of Lugol's solution of iodine to hyperthyroid patients to reduce the metabolic rate, savors of a kind of contradiction.

* Presented before the Division of Medicinal Chemistry at the 79th meeting of the American Chemical Society, Atlanta, Ga., April 7–11, 1930.

Iodized salt has its exponents and its antagonists. Resurveys have not shown the expected results following its use, and Olesen (*5*) considers it harmless but inefficient as a goiter preventive. Neither is he (*5*) willing to recommend the iodization of water supplies, at least in its present state of development. We are hearing a great deal just now about organic forms of iodine and their greater desirability. It is undoubtedly true that iodine combined with fatty acids or amino acids is less rapidly eliminated from the body than simple iodides, but who shall say what organic forms are best? Although di-iodotyrosine has been demonstrated in Gorgonian (*6*) corals, no one has been successful in determining the form in which iodine is combined in oysters, or salmon, or cod-liver oil, foods which are unusually rich in this element. It has been felt that the enrichment of milk with iodine would be a desirable thing in infant feeding. Scharrer (*7*) increased

TABLE I

Effect of Feeding Iodides on the Milk of Dairy Cows*

		Experimental cow		*Control cow*	
Date 1927	*Mg. I as KI*	*Iodine in milk Parts per billion*	*Iodine in urine Parts per billion*	*Iodine in milk Parts per billion*	*Iodine in urine Parts per billion*
Feb. 15	None	45	650	75	540
16	200	...	..	..	...
17	200	170	2,000	..	460
18	200	260	2,650	..	...
19	200	220	3,600	..	...
20	200	300	3,500	..	...
21	200	...	3,000	65	240
22	400	...	..	..	...
23	400	400	5,200	..	440
24	400	450	6,800	..	...
25	400	380	7,300	..	...
26	400	340	7,750	45	330
27	400	430	7,650	..	...
28	600	...	..	..	...
Mar. 1	600	500	8,950	..	750
2	600	580	10,250	..	...
3	600	530	7,000	..	...
4	600	720	7,900	45	140
5	600	1000	11,150	..	...
6	...	700	10,100	..	...
7	...	290	4,120	35	350
9	...	120	1,000	..	...
11	...	80	570	..	360
15	...	45	260	..	...

* From SCHARRER and SCHROPP, *Biochem. Z.*, **213**, 18 (1929).

the iodine content of milk by feeding iodides to cows, but the amount that went into the milk was very much less than that which appeared in the

TABLE II

Distribution of Iodine in Cow's Milk*

Town	*County*	*State*	*Feed*	*Butterfat*	*Dry skim milk*	*Ratio of total iodine in butter to that in skim milk*
Clemson College	....	S. C.	Normal	78	142	0.9
Davis	....	Cal.	Normal	26	164	0.04
Byron Rock River Farm	....	Ill.	Kelp and fish	176	400	0.7
St. Paul	Ramsey	Minn.	Normal	11	....	...
St. Paul	Ramsey	Minn.	Cod-liver oil	36	7,320	0.002
St. Paul	Ramsey	Minn.	Iodized oil,** 100 g. daily	43	65,600	0.0006
St. Paul	Ramsey	Minn.	Iodized salt containing 10% iodine	378	158,000	0.0004
St. Paul	Ramsey	Minn.	4–6 days after discontinuing iodized salt	148	2,800	0.02

* McCLENDON, REMINGTON, VON KOLNITZ, and RUFE, *J. Am. Chem. Soc.*, **52**, 545 (1930).

** Made by adding 20 g. of ICl_3 to a gallon of linseed oil.

urine. McClendon (*8*) has increased the iodine content of milk enormously by feeding cod-liver oil, iodized linseed oil, and iodized salt, but the increase in the fat was negligible compared with the skim milk, and one naturally wonders whether this increase is not largely an excretion of iodides. McClendon found that if milk is rich in iodine due to a normal content of the element in the feed, whether vegetable or fish meal, the ratio of iodine in the milk fat to that in the skim milk is much higher than when it is derived from iodized oils or salt.

Work in South Carolina (*9*) has shown that most root and leafy vegetables grown in a non-goitrous region contain iodine, but that grain is deficient. Some of von Fellenberg's work on foods should be confirmed, and I am quite sure that his results on wheat (*10*) from the United States are too high. No iodine can be recovered from the marsh grass which grows in the tide-waters along the Carolina coast, but the Spanish moss which hangs from the trees contains it. Furthermore, the leaves of such plants as carrots, beets, and turnips contain more iodine (*9*) than the roots. What is the rôle of iodine in agriculture, and what relation does it bear to the desirability of naturally iodized vegetables in goiter prevention? Pfeiffer (*11*) has been able to increase the iodine content of radishes and carrots several hundred times by iodine manuring, and concluded that from 75 to 90% of this iodine is in organic form. What hint does this carry as to agricultural practice in goitrous regions?

What is the biological requirement for iodine? Shall we accept as the criterion the 14 micrograms per day which von Fellenberg (*10*) found necessary to maintain iodine balance in himself, or the 50 micrograms recom-

TABLE III

Iodine Content of Some South Carolina Vegetables

Values are in parts per billion on the dried sample

	Number of samples	*Average iodine content*		*Number of samples*	*Average iodine content*
Green Vegetables			**Fruits**		
Asparagus	26	285	Blueberries	2	206
Green beans	14	210	Dewberries	1	169
Beet tops	3	657	Peaches	3	162
Cabbage	17	263	Pears	1	65
Carrot tops	6	433	Strawberries	5	181
Chinese cabbage	1	300	Tomatoes	8	112
Collards	3	232	Watermelon	1	402
Cucumbers	2	530	**Roots**		
Egg plant	3	187	Artichokes	1	182
Kale	2	278	Beets	9	182
Lettuce	13	912	Carrots	16	213
Mustard	2	224	Irish potatoes	76	211
Okra	3	223	Rutabaga	5	200
Onions	6	222	Sweet potatoes	70	98
Pimentos	1	150	Turnips	13	271
Rape	3	300	**Seeds**		
Spinach	19	692	Cottonseed meal	1	140
Summer squash	7	625	Peas	3	136
Turnip tops	7	376	Oats in hull	1	20
			Peanuts	1	67
			Rye in hull	1	86

mended by some other European investigators, or the 250 micrograms of Marine and Kimball (*12*)?

Granting that some form of iodine feeding is desirable in goitrous areas, to what extent shall it be carried out in any given locality? Goiter surveys on human population are coming to be regarded with more and more distrust. The original study of Olesen (*13*) (Figure 1) on draftees agrees only roughly with the picture as shown by examination of school children (*14*).

TABLE IV

Effects of Iodine Manuring on Radishes and Carrots*

One-half gram of iodine was added in doses of 0.1 gram to each pot, in form of potassium iodide

Plant	*Iodine recovered (parts per billion)*		*Per cent of total iodine in organic form*	*Control experiment*
	Fresh basis	*Dry basis*		*Fresh basis*
Radish leaves	25,347	357,000	96	198
Radish roots	17,814	304,000	86	134
Carrot leaves	20,032	160,000	96	121
Carrot roots	14,842	128,000	94	97

* Modified from PFEIFFER and COURTH, *Biochem. Z.*, **213**, 74 (1929).

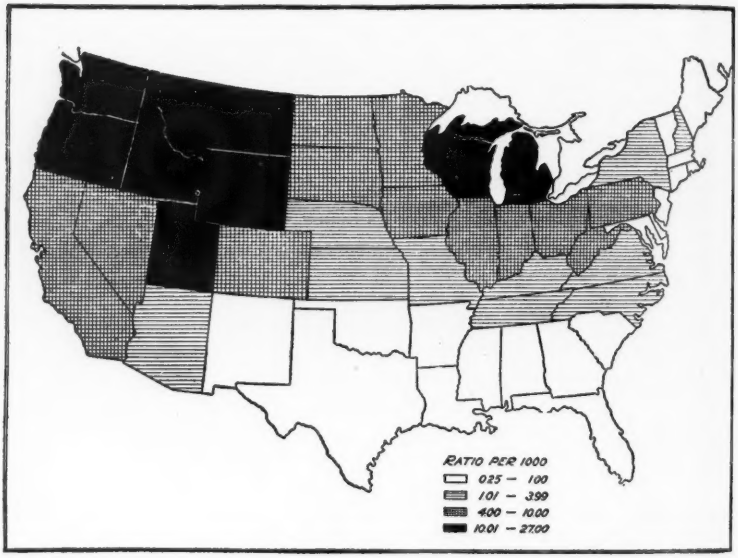


FIGURE 1.—GOITER IN DRAFTED MEN

Map showing ratio of simple goiter per 1000 men examined for military service in each State of the United States during the World War. The rates are based on a total of 2,510,701 examinations. (OLESEN, *U. S. Pub. Health Repts.*, **1927**, p. 3180.)

The criterion as to whether any region is goitrous or not lies not with the population, but with the environment. People move about from place to place, they eat foods from the most distant parts of the country, most remarkable

TABLE V

Goiter in High-School Girls*

	Per cent goitrous		*Per cent goitrous*
Michigan:		*Montana:*	
Houghton County	71	Fergus County	49
Wexford County	56	Carbon	39
Midland County	33	Cascade	34
Malcolm County	26	Big Horn	25
Grand Rapids—Kent County	40	Hill	13
		Ohio, Cincinnati	40
		Colorado	40
		Utah	54
Minnesota:		*Kansas*, Topeka	50
St. Paul	73	*Connecticut*, Average	29
Average of 13 towns	71	Manitoba	43–79

* After MCCLENDON, *Physiol. Rev.*, **1927.**

variations exist in the dietaries of families in the same general circumstances and the same locality, and the extent of the intentional use of iodine in salt or other forms is an unknown factor.

Perhaps a better way would be to map the incidence of goiter in some domestic animal of economic importance, such as the hog. Shepperd (*15*) (Figure 2) has done something along this line in North Dakota, having prepared a map showing the incidence of hairlessness in pigs over a period of six years. But his map reflects not only the incidence of hairlessness more or less accurately, but the diligence of his county agricultural agents in locating and reporting cases.

Is hairlessness more prevalent in pigs farrowed in the spring than in the

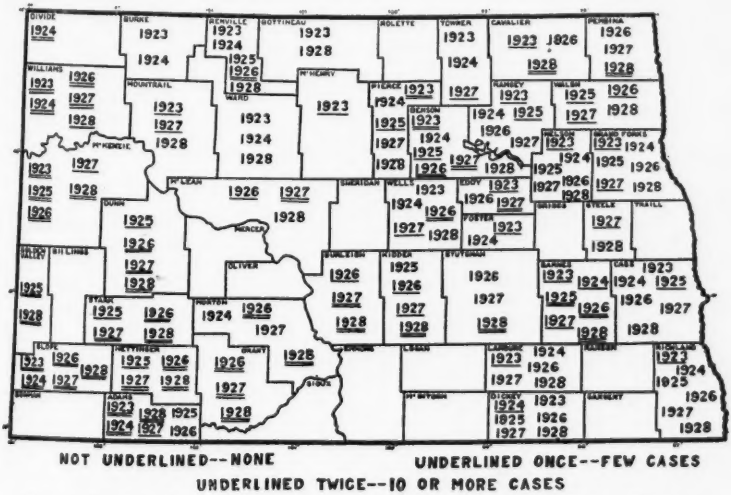


FIGURE 2.—SIX-YEAR INCIDENCE OF HAIRLESSNESS IN PIGS IN NORTH DAKOTA
(SHEPPERD, *N. Dak. Agr. Exp. Sta. Bull.* 230, p. 24.)

fall? No one has attempted to determine, yet Fenger (*16*) showed some time ago that there is a seasonal variation in the iodine content of thyroids from hogs slaughtered in Chicago, and coming presumably from the Great Lakes region mainly, and Kendall (*17*) has shown a similar variation in thyroxin. Fenger is now engaged in a comparative study on this seasonal variation in the Armour plants at Fargo, North Dakota, and Fort Worth, Texas. The results should be interesting. Thyroid examinations on the same group of children, made, say, in September and March, might show some interesting results.

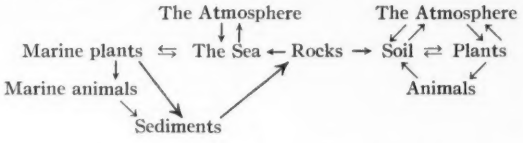
Is this variation climatic or dietary? Does the more severe winter climate of the north make a heavier demand on the thyroid mechanism, with

accompanying depletion of its iodine store, or is the winter diet with its dearth of fresh pasture responsible? Marine (*18*) has been studying the goiter which can be produced in rabbits by feeding winter cabbage. Summer cabbage does not produce goiter in rabbits. Winter cabbage consists of hard, white heads, from which practically all the outer leaves have been removed when taken from winter storage. The heads of summer cabbage, on the other hand, are more open and contain more chlorophyll. What new factor in the etiology of goiter is going to be brought out by Marine's experiments?

If we knew the cycle of iodine in nature we could predict with more certainty what areas would be goitrous. Von Fellenberg (*10*) believes that iodine escapes from the sea both in the free form and mechanically, as sea spray, and is washed down by the rain. This view has received such widespread acceptance that we find the following paragraph in Sherman's (*19*) "Chemistry of Food and Nutrition."

> Sea salt, and therefore the spray which evaporates in the air at the seashore, is relatively rich in iodine; and as this sea-salt dust is carried inland by the wind it gives iodine to the rain-water, the soil water, the soils, and the crops of nearby regions. But regions which, because of too great distance or because of intervening mountains, receive practically none of the airborne sea-spray may contain in their waters and in the crops grown on their soils too little iodine to meet the needs of normal nutrition.

Lunde (*20*) represents the circulation of iodine by the following diagram:



The Atlantic Ocean has been found by several workers to contain about 23 parts per billion of iodine. Relative values for chlorine, bromine, and iodine are as follows:

Chlorine	19,324,000 parts per billion
Bromine	66,000
Iodine	23

According to McClendon (*21*) the pH of sea water is quite constant at about 8.2, and it is hard to understand how free iodine can be evolved from such an alkaline medium. Granting that it is, we are equally at a loss to understand how so active an element can remain free and uncombined in the atmosphere. McClendon has drawn air through absorption bottles for months at a time, and has been unable to find any iodine in air which is free from dust. If we accept the salt spray theory, then we shall have to postulate a gigantic selective adsorptive power of soils for iodine com-

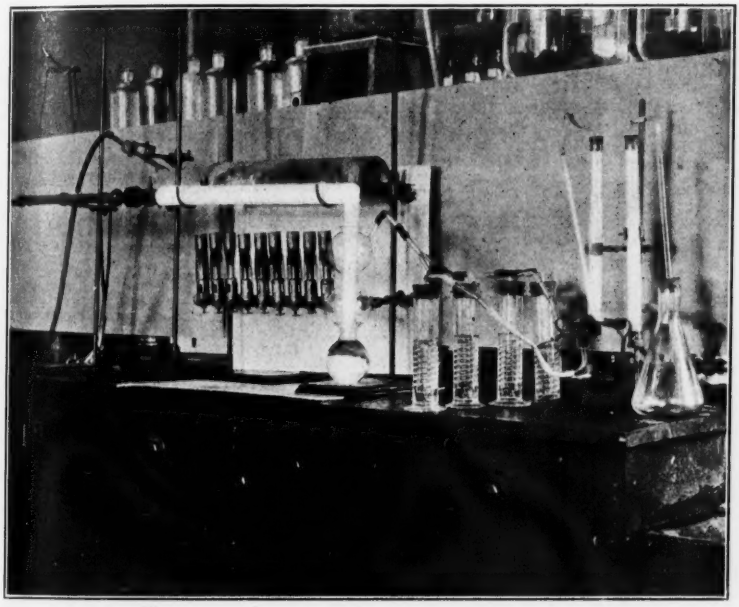


FIGURE 3.—SILICA COMBUSTION FURNACE OF MCCLENDON AS USED IN THE MICRO-ESTIMATION OF IODINE IN ORGANIC MATERIALS

The set-up consists of a metal screw-feed device for introducing the sample; a curved adapter for introducing oxygen; an ell-shaped silica combustion tube; a special absorption vessel into which the end of the silica tube dips; a number of Milligan absorption bottles connected in parallel, and one or two tubes packed with fine glass wool. A curved metal shield lined with asbestos is placed over the furnace during heating.

pounds, since chlorine and iodine will be found in salt spray in the ratio of about a million to one, and nothing like this ratio exists in those soils and surface waters which have been examined. Isochlors show that chlorine is not blown far inland from the sea. In South Carolina (*9*) it has been

TABLE VI

Iodine Content of Potatoes in Relation to Distance from the Sea (in South Carolina)*

Distance from sea	*Number of samples*	*Iodine content in parts per billion dry basis (Average)*
0– 50 miles	19	180
50–100 miles	16	213
100–150 miles	15	223
150–200 miles	15	249
200– miles	4	266

* REMINGTON, CULP, and VON KOLNITZ, *J. Am. Chem. Soc.*, **51**, 2942 (1929).

found that the iodine content of soils (*22*) and crops increases as distance from the sea increases, and we have been led to suggest the archaic rocks of the Appalachians as the source. Von Fellenberg (*10*) found more iodine in archaic rocks than in sedimentary rocks. Lunde (*20*) has suggested that iodine was originally quite uniformly distributed throughout the geosphere, and present inequalities in distribution are due to erosion and washing. Interesting is the suggestion of McClendon (*23*) that iodine is being formed *in situ* by radioactive disintegration, but the work of Millikan (*24*) on the energy required for atomic disintegration renders this improbable.

If soil iodine is derived from primordial rocks, how shall we explain the high incidence of goiter in Idaho, where the soils are mainly volcanic ash, unless the iodine compounds were volatilized and lost by the volcanic heat? The Great Lakes region is goitrous, said to be due to the fact that the soils are mainly of glacial origin. But parts of western North Dakota and eastern Montana were not covered by the ice cap, and are more goitrous than some areas that were. Shepperd (*15*) found highest goiter incidence in the western part of North Dakota, least in the Red River valley. This valley lies in a prehistoric lake bed, and the soils are very heavy clay. Goiter in children and in live stock is less prevalent here than in areas to either the east or the west where the soils are more sandy. What relation does this situation bear to that in South Carolina, where goiter has been found to be less common, and iodine content of vegetation higher, in those areas of more colloidal soils?

Since Wilke-Dorfürt (*25*) has shown that the shells of salt water mussels are rich in iodine, containing as high as 9000 parts per billion, it might be expected that limestone regions would be free from goiter. Kentucky and Tennessee are shown as moderately goitrous on Olesen's map, but no data are available as to whether the limestone regions of those states are more or less goitrous than the balance. The peninsula of Florida, with a soil which is almost pure sand except for the so-called muck or peat areas, should furnish an ideal location to test out the salt spray theory.

Unfortunately, just as goiter surveys are rendered inaccurate by the promiscuous use of iodized salt, studies on vegetation are affected by the use of nitrate of soda from Chile, which may contain a few hundredths of one per cent of iodine. There must be observing physicians living in the South who can recall conditions prior to the use of Chilean nitrate, and if it is an important factor, goiter should have decreased since its introduction.

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Mold Kills Bacteria—May Be New Antiseptic. One of the molds (a *Penicillium*) has been found to kill cultures of some bacteria, notably pus-forming cocci and diphtheria bacilli. This interesting news comes from Dr. Alexander Fleming of the Laboratory of the Inoculation Department, St. Mary's Hospital, London, England. The mold is similar to the common fungus that sometimes spoils oranges and other fruits. Even when cultures are filtered, the resultant liquid which is called "penicillin" is effective. It can be kept for some time if it is neutralized, but if not, it loses its power after from 10 to 14 days at room temperature. It does not affect all bacteria, for instance, the typhoid group is resistant to its action; on the other hand, staphylococci, streptococci, and diphtheria bacteria are killed rapidly. *Penicillin* is not toxic to animals even when given in enormous doses, and it is also non-irritant. It is therefore possible that it may turn out to be a useful antiseptic for combating infections caused by certain pathogenic bacteria.—*Science Service*

Diamonds Scooped Up with Surface Sand. Most of the world's diamond supply no longer comes from mines. They are scooped up with steam shovels. To be sure, the steam shovels get a lot of sand and only a few diamonds, but the diamonds can be sifted out as though they were ordinary pebbles. The discarded sand piles up into a veritable artificial mountain. This gathering of diamonds from the surface is a new development in the obtaining of the world's most valued gems. For centuries diamonds have been laboriously dug from the earth, often at great depths. But recently diamonds were found in great numbers in alluvial deposits in South Africa, and now fully 70 per cent of the world's supply comes from these surface scrapings. The largest stone thus far found in the alluvial workings weighs 85 carats, and others are almost as large.—*Science Service*

LIQUID AMMONIA AS A SOLVENT AND THE AMMONIA SYSTEM OF COMPOUNDS. VII. THE NATURE OF FREE RADICALS, THEIR PREPARATION AND PROPERTIES, AS REVEALED BY STUDIES IN LIQUID AMMONIA SOLUTIONS[1]

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It was pointed out in the earlier articles of this series that liquid ammonia is unique in its ability to serve as a solvent for a large number of different types of compounds. Although it does not surpass water as a solvent for the typical salts, it does, however, excel water as a solvent for organic substances. Liquid ammonia was also shown to be an excellent medium for studying the chemical and physical properties of many substances which do not readily lend themselves to investigation in water. This was found to be particularly true of the alkali and alkaline earth metals as well as the compounds of these strongly electropositive elements with less electropositive elements.

Likewise, many of the free radicals form stable solutions with ammonia while they are incapable of existence in an aqueous medium due to their extreme reactivity. It is true that a great many free radicals are insoluble in liquid ammonia as well as in water. On the other hand, the preparation of some of these compounds has been carried out in liquid ammonia to advantage since the constituents reacting to form the radicals are soluble and produce stable solutions. It is also true that the reactions usually proceed rapidly and quantitatively in this medium. The following pages constitute a brief review of the advances that have been made in this field with liquid ammonia as a solvent.

Types of Free Radicals

It has long been known that certain groups of elements have a tendency to act as units and retain their identity in chemical transformations. So it was that the early investigators in chemistry, in their efforts to establish the science on a quantitative basis, recognized the singular properties of these groups of elements which they termed "radicals." The radical theory held sway for many years but lost its foothold and interest when attempts to explain all chemical combinations were found to be futile. The advent of radicals as definite entities in organic chemistry created a more general interest in the study of all types.

A radical is nothing more than a group of elements acting as a unit. In other words, the group of elements behaves as a single element in a

[1] Previous papers in this series have appeared as follows: I, THIS JOURNAL, **5**, 664–70 (June, 1928); II, *ibid.*, 828–35 (July, 1928); III, *ibid.*, **6**, 20–35 (Jan., 1929); IV, *ibid.*, 441–50 (Mar., 1929); V, *ibid.*, **7**, 981–99 (May, 1930); VI, Part I, *ibid.*, 1291–9 (June, 1930); VI, Part II, *ibid.*, 1602–16 (July, 1930); VI, Part III, *ibid.*, 1850–8 (August, 1930).

transformation of matter. Typical examples are the sulfate, nitrate, ammonium, perchlorate, triphenylmethyl, thiocyanogen radicals, etc. They are not to be confused with the ions of these groups; free radicals are neutral substances.

Since these groups of elements function as individuals, it is natural to predict their properties as being very closely allied to the properties of the elements themselves. The elements have been classified according to their affinity for the electron. The free radicals have been classified in a like manner.[2] In the first group we have the strongly electropositive radicals with the tetramethylammonium group as an excellent example. It will be expected to resemble the alkali metals in its properties, both chemically and physically. Its affinity for the electron will likewise be small as is true of the alkali metals. Then there will be a group of radicals having a pronounced affinity for the electron and resembling those elements which are termed as strongly electronegative. The thiocyanogen radical is a typical example of the second kind. The third class will necessarily include those radicals that have neither a pronounced affinity for the electron, nor a tendency to lose it. They will act either one way or the other depending upon their environment; in the presence of a strongly electropositive element or group, they will function electronegatively or acquire the electron, while in the presence of a strongly electronegative element or group, they will lose the electron and act as an electropositive constituent. For this reason the third class has been termed as "amphoteric." Triphenylmethyl and trimethyl tin are typical examples of the last class.

The Strongly Electropositive Radicals

One of the simplest groups of this type is the ammonium group. Ruff[3] and Moissan[4] claimed to have prepared this group by the electrolysis of ammonium salts dissolved in liquid ammonia at low temperatures. Palmaer[5] carried out the same experiment but was unable to reproduce the results of Ruff and Moissan. Kraus[6] also attempted to prepare the free ammonium radical in a like manner but his results agreed with those of Palmaer in being negative. It is quite probable that the free ammonium radical is formed in this experiment but the results indicate that it is very unstable.

The substituted ammonium salts have provided more promising results. Palmaer[5] electrolyzed tetramethyl- and tetraethyl-ammonium salts dis-

[2] Kraus, "Radicals as Chemical Individuals," Columbia University Press, New York, 1927. See also THIS JOURNAL, **7**, 981–99, (May, 1930).

[3] Ruff, *Ber.*, **34**, 2604 (1901).

[4] Moissan, *Compt. rend.*, **133**, 715 (1901).

[5] Palmaer, *Z. Electrochem.*, **8**, 729 (1902).

[6] Kraus, *J. Am. Chem. Soc.*, **35**, 1732 (1913).

solved in liquid ammonia with startling results. During the process of electrolysis he noticed around the cathode a distinct blue color characteristic of an alkali or alkaline earth metal dissolved in liquid ammonia. We have excellent evidence for the fact that the blue color characteristic of metal solutions is due to the electron associated with ammonia molecules. The metal ions, that is, those of sodium, potassium, lithium, calcium, etc., are colorless in this medium. Likewise, it is reasonable to ascribe the blue color, obtained in the electrolysis of the tetramethylammonium salt, to the free electron associated with solvent molecules. The process of electrolysis therefore consists of the migration of the tetramethylammonium ion to the cathode where it acquires the electron to form the tetramethylammonium group. This group is metallic in appearance and chemical behavior, it dissolves in liquid ammonia to give on dissociation the normal positive ion and the electron combined with solvent molecules. Both the chemical and physical properties of these strongly electropositive radicals are closely allied to those of the strongly electropositive elements.[7]

The results of Palmaer have been repeated and confirmed by Kraus,[6] who, in addition, prepared the free tetrapropylammonium radical.

Quantitative data concerning the preparation of tetramethylammonium were first brought to bear by McCoy and Moore.[8] They electrolyzed a saturated solution of tetramethylammonium chloride in absolute alcohol using a platinum anode and a mercury cathode. The experiment was carried out at $-10°$. The salt ionizes in the alcohol as follows:

$$(CH_3)_4NCl = (CH_3)_4N^+ + Cl^-$$

and, accordingly, during the process of electrolysis, the cation collects in the mercury after being discharged at the pole. What was obtained was an amalgam of free tetramethylammonium. The amalgam appeared as a stiff mixture of shining, white, silvery crystals which were decidedly metallic. It was found to be moderately stable in alcohol but exceedingly reactive with water.

The electrode potential of the free radical dissolved in mercury was determined and compared with that of sodium and also potassium under the same conditions. The radical was found to be more electropositive than sodium and less electropositive than potassium. Many other reactions were carried out by McCoy to determine the nature of the group; in all cases it was found to resemble the alkali metals closely.

Other free metallic radicals have been studied in liquid ammonia. Kraus[6] has electrolyzed several alkyl mercury halides in this medium and has found the methyl, ethyl, propyl, and amyl mercury radicals to be

[7] See THIS JOURNAL, **6**, 20–35 (Jan., 1929); and *ibid.*, **7**, 981–99 (May, 1930).

[8] McCoy and Moore, *J. Am. Chem. Soc.*, **33**, 273 (1911).

sufficiently stable at low temperatures, $-60°$, for carrying out investigations on their properties. The more complex the alkyl group, the more unstable is the free radical. The general reaction may be expressed as follows:

$$RHgX = RHg^+ + X^-$$
$$X^- = X + \epsilon^-$$
$$RHg^+ + \epsilon^- = RHg$$

These alkyl mercury groups have been shown to possess metallic properties and thus have been properly classified with the more electropositive radicals. It may be stated, however, that they are by no means as strongly electropositive as the substituted ammonium groups. They form a connecting link in an electro-affinity series between the strongly electropositive radicals and the amphoteric radicals.

The Strongly Electronegative Radicals

The strongly electronegative radicals have a pronounced affinity for the electron and resemble the strongly electronegative elements. Only a few of these radicals have been isolated and they are known to exist in the dimolecular state. Thus we have thiocyanogen, $(SCN)_2$; cyanogen, $(CN)_2$; selenocyanogen, $(SeCN)_2$; oxycyanogen, $(OCN)_2$; and azidocarbondisulfide, $(SCSN_3)_2$. They are not free radicals in the same sense as is triphenylmethyl, trimethyl tin, and undoubtedly tetramethylammonium since they do not exist in the mono-molecular state. They have been termed free radicals since they remain unchanged in a series of chemical reactions. They[9] resemble the strongly electronegative elements such as chlorine, bromine, etc., which also exist, in the free state, in a dimeric condition.

The halogens are known to react with ammonia (ammonolysis) to produce ammono acids. As an example, we may subject chlorine to the action of ammonia:

$$Cl_2 + 2NH_3 = NH_4Cl + ClNH_2.$$

Ammonium chloride is an acid in liquid ammonia, corresponding to hydrochloric acid in the water system, while chloramine corresponds to hypochlorous acid. Since the electronegative free radicals, as they have been called, closely resemble the electronegative elements in their properties, it is to be expected that they also would undergo ammonolysis in a liquid ammonia medium. This being the case, ammonia is not practical as a medium for studying these groups. It may be added, though, that many reactions involving compounds containing these radicals have been carried out in ammonia to advantage.

[9] For a complete discussion of these electronegative radicals see Walden and Audrieth, *Chem. Rev.*, **5**, 339 (1928).

Amphoteric Free Radicals

The radicals of the third class have been termed amphoteric since in a series of electroaffinities they lie intermediately between the strongly electropositive and the strongly electronegative radicals. Such a series does not offer any sharp lines of distinction; it is composed of radicals of all types that form a continuous series. Accordingly, the amphoteric radicals exploit a wide range in the series and exhibit properties that are characteristic of the two extreme types. In other words, they will combine with the strongly electropositive elements to form salts and they will also combine with the strongly electronegative elements to produce substances which are not salt-like in nature.

From a consideration of the properties of amphoteric elements[10] it would be predicted that the amphoteric radicals would contain these same elements as central atoms. In general, elements of the third, fourth, and fifth groups of the periodic system function as central atoms. The chemical properties of the radicals as a whole involve the chemistry of the central atoms almost entirely; the attached groups merely make up the radical and usually do not undergo changes in a series of chemical reactions.

For the sake of brevity we shall consider here only those radicals containing a fourth group element as the central atom. Thus we shall have the elements carbon, silicon, germanium, tin, and lead in combination with alkyl or aryl groups producing larger groups that appear to act as units and retain their identity throughout the course of a series of chemical changes.

The trivalency of carbon was shown by Gomberg[11] in 1900 when he prepared triphenylmethyl by the reduction of triphenylmethylchloride by molecular silver in benzene solution:

$$2(C_6H_5)_3CCl + 2Ag = (C_6H_5)_3C - C(C_6H_5)_3 + 2AgCl.$$

The hexaphenylethane was found to dissociate to free triphenylmethyl in benzene solution and to exhibit properties indicative of an unsaturated bond:

$$(C_6H_5)_3C - C(C_6H_5)_3 = 2(C_6H_5)_3C.$$

A powerful reducing medium is obtained when an alkali metal is dissolved in liquid ammonia. The metal ionizes in this medium to give the normal alkali metal ion and the electron associated with solvent molecules. The electron is thus free to combine with any constituent that

[10] THIS JOURNAL, **7**, 981–99 (May, 1930).

[11] Gomberg, *J. Am. Chem. Soc.*, **22**, 757 (1900); for a complete discussion of free organic radicals see Gomberg, *Chem. Rev.*, **1**, 91 (1924).

has a tendency to acquire it. Triphenylmethyl chloride is reduced by sodium in liquid ammonia as follows:[12]

$$(C_6H_5)_3CCl + 2Na = NaCl + (C_6H_5)_3CNa$$

The sodium salt of triphenylmethyl is a typical salt. It is highly ionized in liquid ammonia, conducts the electric current with great facility, and slowly undergoes ammonolysis. It may be compared to sodium hydride, NaH, which is a salt. Ammonolysis occurs since it is a salt of an extremely weak acid, triphenylmethane:

$$(C_6H_5)_3CNa + NH_3 = (C_6H_5)_3CH + NaNH_2$$

In this reaction sodium amide, an ammono base, and triphenylmethane, the acid, are produced. The acid is undoubtedly associated with ammonia.

The high conductivity values of solutions of the sodium salt dissolved in liquid ammonia show that the compound is highly ionized:

$$(C_6H_5)_3CNa = Na^+ + (C_6H_5)_3C^-$$

When the sodium salt is reacted with triphenylmethyl chloride in liquid ammonia, free triphenylmethyl is formed:

$$(C_6H_5)_3CNa + (C_6H_5)_3CCl = (C_6H_5)_3C - C(C_6H_5)_3 + NaCl$$

The free radical, or the associated compound hexaphenylethane, is very insoluble in ammonia. Under such conditions it has been impossible to make any determinations of the molecular weight of the substance in solution; however, its nature is brought out when it is subjected to the action of metallic sodium:

$$(C_6H_5)_3C-C(C_6H_5)_3 + 2Na = 2(C_6H_5)_3CNa$$

The associated molecule readily reacts with the halogens, (not in liquid ammonia but in the usual organic solvents) to give the corresponding halides:

$$(C_6H_5)_3C-C(C_6H_5)_3 + Cl_2 = 2(C_6H_5)_3CCl$$

Triphenylmethyl chloride is not a typical salt, it resembles the halogen acids closely in its properties. Hydrochloric acid is known to be an exceedingly weak electrolyte in the pure state and a good conductor of the electric current in water-like solvents. Triphenylmethyl chloride likewise is a poor conductor in the fused state but a fairly good conductor in alcohol. Again we may ascribe these properties to the formation of complexes in solution.

The metallic elements of the fourth group of the periodic system, in combination with alkyl and aryl groups, produce radicals that are similar in nature to the carbon radicals. Compounds of tin have been studied more extensively than those of silicon, germanium, and lead, and offer

[12] Kraus and Kawamura, *J. Am. Chem. Soc.*, **45**, 2756 (1923).

excellent examples from the standpoint of liquid ammonia. The free trimethyltin[13] radical has been obtained by the reduction of trimethyltin halides with metallic sodium in liquid ammonia. The reaction proceeds rapidly and quantitatively as follows:

$$(CH_3)_3SnCl + Na = (CH_3)_3Sn + NaCl$$

Trimethyltin is a solid at ordinary temperatures, melts at 23°, and boils at 182°. Molecular weights carried out in benzene solution at the boiling point show that the substance is present in the monomolecular form, that is, in the form of free trimethyltin. The extent of dissociation of the hexamethylstannoethane is dependent upon the concentration. At lower concentrations, the molecular weight corresponds well with that of the free group; a value of 171 is obtained as against 164 for complete dissociation. As the concentration increases, the molecular weight increases until a value corresponding to the dimolecular form is obtained. The latter is realized when the concentration of the solute is about 0.15 moles per liter of benzene.

Trimethyltin is readily oxidized in air to the corresponding oxide, $2(CH_3)_3Sn + {}^1/_2O_2 = (CH_3)_3SnOSn(CH_3)_3$. This reaction differs from the analogous one with triphenylmethyl in that the latter gives the peroxide,

$$2(C_6H_5)_3C + O_2 = (C_6H_5)_3COOC(C_6H_5)_3$$

Trimethyltin also reacts with sulfur, in a manner similar to the oxygen reaction, to produce trimethyltin sulfide, $(CH_3)_3SnSSn(CH_3)_3$. Reactions have been found to take place between trimethyltin and metallic halides. With mercuric chloride in ether, a rapid reaction occurs with the formation of trimethyltin chloride and metallic mercury. This shows that the radical is sufficiently electropositive to reduce mercuric chloride.

Trimethyltin chloride reacts with the sodium salt of trimethyltin to give the free radical in a manner entirely analogous to the reactions found in the case of the triphenylmethyl derivatives,

$$(CH_3)_3SnCl + (CH_3)_3SnNa = NaCl + 2(CH_3)_3Sn$$

The electroaffinities of these radicals are better realized in the two following reactions.[14]

$$(CH_3)_3SnCl + (C_2H_5)_3SnNa = NaCl + (CH_3)_3SnSn(C_2H_5)_3 \quad (1)$$
$$(CH_3)_3SnNa + (C_2H_5)_3SnCl = NaCl + (C_2H_5)_3SnSn(CH_3)_3 \quad (2)$$

In the first reaction trimethyltin chloride is treated with the sodium salt of triethyltin, while in the second, triethyltin chloride reacts with the sodium salt of trimethyltin. The products of both reactions are

[13] Kraus and Sessions, *J. Am. Chem. Soc.*, **47**, 2361 (1925).
[14] Kraus and Bullard, *ibid.*, **48**, 2131 (1926).

the same regardless of the condition of the radicals before reaction proceeds. This immediately shows that the radicals are truly amphoteric, that they do not have any definite tendency to acquire or lose the electron pair.

The aryl derivatives of tin behave much like the alkyl compounds.[15] A considerable amount of work has also been carried out with the mixed alkyl, mixed aryl, and mixed alkyl-aryl radicals of tin.[16] Space does not permit of a discussion of their properties here.

Radicals containing tin with a valence of two have been studied in liquid ammonia. When dimethyltin bromide is reduced with sodium in ammonia the free dimethyltin radical results,[17]

$$(CH_3)_2SnBr_2 + 2Na = 2NaBr + (CH_3)_2Sn$$

The dimethyltin group has a great tendency to polymerize to more complex compounds. The degree of polymerization is not known and appears to vary with the conditions of the experiments followed. This fact is evidenced by the variation in the properties of products formed in the different methods of preparation. Krause[18] has succeeded in preparing the free diphenyltin radical in organic solvents. It is quite probable that the dimethyltin radical also is present when prepared in liquid ammonia, although it does have a marked tendency to polymerize.

Dimethyltin reacts readily with metallic sodium in ammonia to form the disodium salt, first, of tetramethylstannoethane, and second, of dimethyltin according to the equations:

$$2(CH_3)_2Sn + 2Na = NaSn(CH_3)_2Sn(CH_3)_2Na \quad (1)$$
$$NaSn(CH_3)_2Sn(CH_3)_2Na + 2Na = 2Na_2Sn(CH_3)_2 \quad (2)$$

These salts are readily soluble in ammonia and are excellent electrolytes. They have proved useful in the synthesis of higher derivatives of organotin compounds in that they react readily with the halides of tin radicals of the type under discussion.

Radicals containing silicon, germanium, and also lead have been investigated in liquid ammonia. In certain instances difficulties have been encountered due to the ammonolysis of the constituents used in the preparation of the radicals and their derivatives. The above-described preparations are merely suggestive of the nature of the reactions that have been studied in ammonia. They are typical examples of a large number of different types of reactions.

[15] Chambers and Sherer, *J. Am. Chem. Soc.*, **48**, 1054 (1926).

[16] Bullard and Robinson, *ibid.*, **49**, 1368 (1927); Bullard and Vingee, *ibid.*, **51** 892 (1929).

[17] Kraus and Greer, *ibid.*, **47**, 2568 (1925).

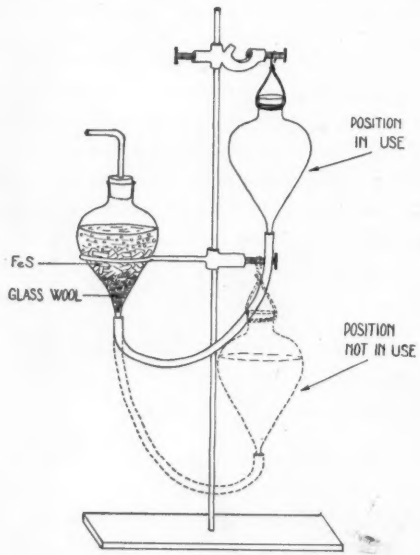
[18] Krause, *Ber.*, **53**, 173 (1920).

In concluding this series of articles concerning the solvent properties of liquid ammonia the writers want to express their appreciation for the many helpful suggestions rendered by Dr. Franklin and Dr. Kraus. We are also greatly indebted to Dr. F. W. Bergstrom of Stanford University, Dr. W. M. Burgess of the University of Cincinnati, Dr. R. H. Bullard of Hobart College, Dr. L. S. Foster of Brown University, and Dr. H. H. Strain of the Carnegie Institute of Washington, Stanford University, for criticisms and suggestions.

ANOTHER HYDROGEN SULFIDE GENERATOR

W. A. MANUEL, OHIO WESLEYAN UNIVERSITY, DELAWARE, OHIO

A small hydrogen sulfide generator, constructed from two 250-ml. gas-leveling bulbs properly connected and mounted on an ordinary ring stand, as indicated in the accompanying diagram, has the following characteristics which make it suitable for use in the general and analytical laboratories.



1. It is simple, and broken parts are easily replaced.
2. It is compact, portable, and easily cleaned.
3. A gas-washing bottle may be clamped to the same stand and thus become a part of the unit.
4. If the gas is used in the "bubbling through" method, the action of the generator may be stopped quickly by lowering the reservoir bulb.
5. If the gas is used by the "closed flask" method, the action of the generator becomes automatic, and a slight pressure can be maintained.
6. A generator of this type may be used for the production of other gases, for which a Kipp is ordinarily used.

The amount of acid charged into a generator of this type should not be greater than half the capacity of the reservoir bulb.

THE DISCOVERY OF SYNTHETIC ALIZARIN*

LOUIS F. FIESER,† BRYN MAWR COLLEGE, BRYN MAWR, PENNSYLVANIA

Few scientific discoveries appeal so strikingly to the imagination as the first laboratory preparation of one of the oldest and most beautiful of natural dyestuffs. The problem was difficult, the manner in which its solution was accomplished was altogether remarkable, and the importance of the discovery to the development of organic chemistry and to agricultural and chemical industries is too great to be estimated at all adequately. When one considers the experiences of the chemists who achieved this synthesis, the outstanding feature of the discovery lies in the manner in which fortune favored their entire series of investigations. It in no way detracts from the brilliance of Pasteur's resolution of racemic acid that his first observation was purely accidental, and it is with no intention of disparaging the accomplishments of Graebe, Liebermann, Caro, and Perkin that we wish to call attention again to this aspect of their work, but rather out of pure admiration for the way in which these great men availed themselves of every opportunity which chanced their way.

Berichte, 61, 11 (1928)

CARL GRAEBE
1814–1927

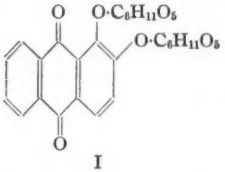
The problem of accomplishing the artificial preparation of alizarin must

* The illustrations of Liebermann (p. 2621) and of Caro (p. 2627) accompanying this article are ones which were used in connection with an article by R. E. Rose on "Growth of the Dyestuffs Industry: The Application of Science to Art," J. CHEM. EDUC., 3, 968, 973–1007 (Sept., 1926). Reference to this article will disclose other pertinent portraits and valuable information.

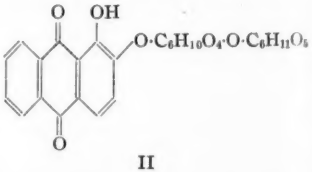
† Now at Harvard University, Cambridge, Massachusetts.

have made a strong appeal to the early organic chemists on account of the antiquity and importance of the dyestuff. The art of dyeing with the red substance which occurs in the root of the madder was known in ancient Egypt, in Persia, and in India. Mummies have been found wrapped in cloth dyed with the so-called Turkey Red, and in many cases the color is still in excellent condition. For many centuries madder and indigo were the leading dyestuffs of the world. The madder, a plant of the genus *Rubia tinctorum*, is native to Asia, and it was at first grown chiefly around Adrianople, Smyrna, and the Isle of Cyprus. As an article of commerce, it became available in European countries as early as the year 700, and the cultivation of the plant was carried into Italy as a result of the Crusades. Madder appeared in Holland and Germany in the 15th century and in Alsace in the 16th century. The best variety is believed to have been introduced at Avignon in 1760. It flourished particularly well in Alsace and in Provence. By the end of the 17th century the annual exportations had mounted to about 2,500,000 kg. The use of the dyestuff thus became very widespread and the cultivation of madder acquired a considerable economic importance to France. The production fell off only temporarily during the Revolution and the First Empire, and it is recorded that Louis Philippe, in order to stimulate the growing of the plant in France, equipped his armies with breeches dyed with Turkey Red, a practice of very dubious military value which was only abandoned in 1914.

The dyestuff was used in the form of a fine powder made by drying and grinding the roots of the plant. The commercial material contained about 1% of alizarin. This substance does not occur in the living plant in the free state, but in combination with two molecules of glucose, in the form of a compound known as ruberythrinic acid. The acid is either a diglucoside, I, or a mono-bioside, II. The latter formula is regarded as the more prob-

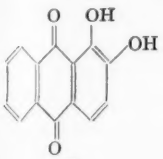


I

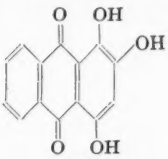


II

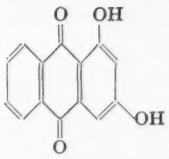
able, but it has not yet been possible to settle the point by the synthesis of ruberythrinic acid. The hydrolysis of the glucoside to alizarin, III, is brought about in madder preparations by the action of an enzyme which occurs in the plant, or it may be effected by the use of a mineral acid. Though alizarin is the chief coloring matter present in the madder, it is accompanied by small amounts of purpurin, IV, purpuroxanthin V, and by methyl and carboxylic acid derivatives of these two substances.



III

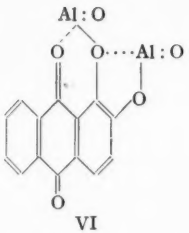


IV

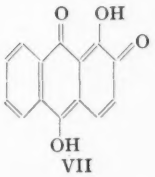


V

Alizarin has very little affinity for cotton unless the fiber is first treated with a suitable mordant. When a metal hydroxide such as aluminum hydroxide, which has colloidal properties, is precipitated on cotton by hydrolyzing an aluminum salt with which the cloth is impregnated, a very firm combination between the metal and the fiber results. The alizarin molecule is now capable of reacting with the metal hydroxide, probably by loss of water between the hydroxyl groups of the two substances, and in that way becomes held, indirectly, to the fiber. The combination between the mordant and the dye appears to involve both primary and secondary valences, and the structure of the alizarin "lake" is usually represented by means of a formula such as VI. Attempts to account for the color phe-



VI



VII

nomena on the assumption of the tautomeric form of alizarin, VII, have not met with great success, and it is generally considered that such a tautomerization occurs only under rare and unusual circumstances.

The actual process of dyeing with alizarin is not at all easy. The older formulas specify treatments of the cloth with Turkey Red oil, a rancid vegetable oil. This is followed by a de-greasing process, treatment with tannin, soaking in aluminum sulfate solution, and steaming. The dye is then applied in the form of a fine aqueous suspension, but the color is somewhat dull and must be enlivened, or "shaded off," in a soap bath containing a little tin salt. In later processes some improvements were effected by substituting sulfonated castor oil for the Turkey Red oil, and by altering other details, but this type of dyeing has always been very complicated and the best results are only obtained by controlling a great many, rather uncertain, factors. The most successful formulas have been passed down from father to son and kept as closely guarded secrets. In the

hands of such experts, however, dyeing with madder has given rise to some remarkably beautiful color effects. Though the dyestuff has been used most frequently with an aluminum mordant to produce dyeings in red, the madder colorist is by no means limited to this one color. Alizarin forms lakes with many different metals and these salts present a wide variety of color. Thus different effects are produced by mordanting the cloth with aluminum, iron, chromium, or tin, or with various combinations of metals. The colors for which madder has been employed most extensively are: red, rose, black, violet, lilac, and dark brown. Another variation, though one which is not easily controlled in the natural product, arises from the fact that the relative proportion of the dyes which occur with alizarin in the madder root varies somewhat with the season, the weather, and the locality. Thus even a small amount of purpurin has a quite noticeable effect upon the color.

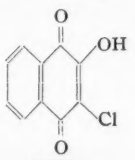
Because of the extraordinary fastness of the dye, and the great beauty and variety of the colors, one can easily understand how madder came to be prized so highly. In his famous "*Traité des matières colorantes*" of 1867, Schutzenberger[1] expressed the view that the only substance which could possibly dethrone madder would be the artificially prepared active principle of madder. If, contrary to this prediction, synthetic alizarin is less favored today than many other dyes, it is not because alizarin is inferior in fastness or color to the new dyes, but it is largely because the newer substances can be applied by much simpler processes and without the special knowledge which is required in working with alizarin.

Though Schutzenberger's vision of a synthetic alizarin was realized very soon after the publication of his book, it was no less than forty-three years after the isolation of the substance that the synthesis was accomplished. Several early investigators attempted to isolate the principle of madder without great success, but the substance was finally obtained in a state of great purity by Robiquet and Colin in 1826. The substance, which forms orange-red crystals of rare beauty, was given the name alizarin from *alizari*, the oriental name for madder derived from the Arabic *azara*, meaning to press or squeeze. The samples were purified by sublimation and carefully analyzed by Robiquet in 1835. The analytical results of this worker are in excellent agreement with the figures calculated from the true formula, $C_{14}H_8O_4$, but the atomic weight of carbon was not known accurately in those days and the French investigator was led to the erroneous conclusion that alizarin is $C_{37}H_{48}O_{10}$. Having isolated the substance in a pure condition, having analyzed it and established what he considered to be the correct formula, he had, according to the standards of the time, completely solved the alizarin problem. The ideas of isomerism

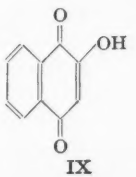
[1] See "Paul Schutzenberger," by Tenney L. Davis, J. CHEM. EDUC., **6**, 1403–14 (Sept., 1929).

and of synthesis had not yet developed, and the science was still in the purely analytical phase initiated by Lavoisier.

Following Robiquet, a number of other investigators reported analyses of the important dyestuff, but there was little agreement in the results. The alizarin content of madder is not great and the separation of the dyestuff from the other substances present is not an easy matter. Thus in spite of the enormous quantities of madder produced, alizarin remained a very rare chemical and it is probable that few investigators obtained it in a completely pure form. Varying figures were obtained for the carbon content and formulas indicating from fourteen to sixty carbon atoms were proposed. The problem was very confused and some writers considered that madder contains a large number of individual compounds corresponding to the different sets of analyses. This conclusion, to be sure, was contested in 1848 by Schunk, who supported the claim that other workers had analyzed impure preparations by excellent experimental work of his own. His results agreed well with Robiquet's figures, and he deduced a formula, $C_{14}H_{10}O_4$, which is very close to the true one, $C_{14}H_8O_4$. But Schunk's formula, however much it merited attention, made little impression on the chemical world and it was rejected, oddly enough, on account of a discovery made by Schunk himself in 1848. He found that alizarin yielded on oxidation a substance to which he gave the name "alizarinic acid," but which was subsequently found to be identical with phthalic acid. The formation of phthalic acid from 1,2-dihydroxyanthraquinone seems so clear to us today that the train of reasoning which was prompted by this discovery appears altogether remarkable. Phthalic acid, argued Wolff and Strecker in 1850, is formed by the oxidation of naphthalene, a ten-carbon substance; since alizarin also yields this acid, the dyestuff must also have a ten-carbon skeleton and it is thus a derivative of naphthalene. This conclusion appeared to be well supported by the fact that alizarin is similar in properties to chloro-naphthalenic acid, which Laurent had prepared from naphthalene. Both compounds give a variety of color reactions with alkalies and with concentrated sulfuric acid, they are both reducible, and they yield phthalic acid on oxidation. There is indeed a structural similarity between the two substances, but the similarity is not that they are both naphthalene derivatives, as Wolff and Strecker supposed, but rather that they are both hydroxyquinones. Laurent's compound has the structure of VIII.



VIII



IX

Wolff and Strecker, however, were firmly convinced of the correctness of their hypothesis and they assigned to alizarin the formula $C_{10}H_6O_3$, which agreed fairly well with some of the analyses which had been reported, in order to express the similarity to chlor-naphthalenic acid, which is $C_{10}H_5O_3Cl$. In short, Laurent's compound was regarded as chloro-alizarin. Naphthalenic acid, IX, which has the structure which they would have assigned to alizarin, was then unknown. All efforts to prepare alizarin by reduction of the chloro compound were of course unsuccessful, but the two investigators attributed this failure to accidental circumstances rather than to any fault of the theory, and they considered that the synthesis of alizarin was assured and that it was only a question of finding a suitable experimental method. They thought that it would be possible to prepare it directly from naphthalene, and they even discussed the possibility of producing the dyestuff on a commercial scale. It is unfortunate that their enthusiasm led them to an injudicious evaluation of the analytical results available, for the formula which they proposed has a carbon content nearly one per cent lower than that indicated by the best analyses on sublimed material. In spite of this discrepancy, the views of Wolff and Strecker were accepted quite generally and for nearly twenty years alizarin was regarded as a derivative of naphthalene. When Martius and Griess discovered naphthalenic acid, IX, in 1865 they described it as an isomer of alizarin, for it differed from this compound.

No further experimental facts bearing on the problem came to light until Graebe and Liebermann commenced their famous series of investigations in 1868. In order to appreciate their work fully it is well to reconstruct a picture of the chemical world at that time. In 1868 organic chemical theory was in a state of transition. The older ideas were still being advocated in the "schools" of the famous masters. But Geheimrat Prof. Dr. Friederich Wöhler of Göttingen, Geheimrat Prof. Dr. Freiherr Justus von Liebig, and Sénateur Jean Baptiste Dumas of Paris had all passed their sixty-fifth year and their influence was rapidly decreasing. Though somewhat younger, Geheimrat Prof. Dr. Robert Bunsen of Heidelberg should be classed with this distinguished trio. Of the men in their early fifties, Kolbe had just accepted a call to Leipzig and the days of his experimental work were largely over, Wurtz of Paris had already made his greatest contributions, while Hofmann really belongs to two periods, for this great experimentalist and leader was nearly as active in the years following 1868 as he had been up to that time. Each of these six great masters had exerted a profound influence on the development of the new science, and they numbered among their students practically all of the productive investigators of the world; but, with the exception of Hofmann, the day of their greatest creative activity and of their influence on the thought of the period had passed. Even Berthelot, at the age of forty-one, had passed through

the peak of his activity in the field of organic chemistry and he now occupied the post of Minister of Education in France.

The moving spirit of the day was that of August Kekulé von Stradonitz. Kekulé,[2] now in his fortieth year, was at the University of Bonn, having transferred from Geneva in 1858. His classical structural theory had been announced in that same year, and the first volume of his famous "*Lehrbuch*" appeared in 1859. His new ideas, which eventually led to a clear conception of valence and to a general adoption of structural formulas, created widespread interest and his views found support which was more than adequate to sustain the attack of some of his older colleagues. His most significant achievement came in 1865 when Kekulé published in a lengthy *Annalen* paper his epoch-making theory of the structure of benzene. Up to this time the aromatic compounds had received relatively little attention and no views regarding their constitution had been advanced. There was no doubt as to the importance of the aromatic substances, particularly to the young dyestuff industry, and the delay in unraveling the benzene problem was due only to the difficulty in finding a suitable solution. The brilliance of the achievement of Kekulé is derived partly from the fact that he solved a problem which had baffled many ingenious minds, but it is of equal importance that his solution was characterized by its great simplicity. The benzene hexagon is comparable to the carbon tetrahedron of van't Hoff. In each case a very large number of perplexing facts were explained by means of a theory which is so rational and clear that it may be described by means of a simple diagram. Each theory had to weather the storm of Kolbe's bitter attack, and each has received unexpected experimental support from modern physics, and has been retained in only slightly modified form into the present era.

The new theory was received with great enthusiasm and by 1868 numerous investigators were busily engaged in working out structural problems according to Kekulé's extended ideas of valence. A few of Kekulé's contemporaries, men in the early forties, shared in this work and mention may be made of Erlenmeyer of Heidelberg, Stanislao Cannizzaro, then at Palermo, and Friedel of Paris in this connection. On the other hand, the group in London, which consisted of Hofmann's successor Frankland, the industrialist Griess, and Williamson, were busy following their own programs based upon their recently discovered reactions. It thus remained largely for a still younger group to explore the vast field which suddenly had been illuminated by Kekulé's genius. Kekulé was a man of delightful personality and his charm and wit were no small factors in causing even some of the Kolbe-trained men to regard themselves before long as belonging to the "Kekulé school."

[2] See "August Kekulé," by L. Darmstaedter and R. E. Oesper, J. CHEM. EDUC., 4, 697–702 (June, 1927).

Berlin was the center of this active group of thirty-year old chemists who plunged with enthusiasm into problems of structural chemistry. Adolf Baeyer was the leader. At the age of thirty-three, Baeyer had completed an important work on uric acid and he had commenced his brilliant indigo work. In 1860 he had founded an organic laboratory at the *Gewerbe-Akademie*, which later grew into the present *Technische Hochschule*. Since the conditions in Hofmann's laboratory were not very satisfactory for independent work on the part of the assistants, many able men were attracted to the laboratory of the successful young experimenter who cordially encouraged them to undertake problems of their own. Baeyer played a leading part in the founding of the *Deutsche Chemische Gesellschaft*, of which the distinguished August Wilhelm von Hofmann was the first president. The organization took place on November 11, 1867, with a membership of one hundred and three. The society, which now claims over five thousand members, probably has done more for the science of organic chemistry than any similar organization in the world. Its great success may be attributed to the careful plans formulated by Hofmann, Baeyer, and their colleagues.

Among the contemporaries of Baeyer who, in or near their early thirties, were active followers of the new school in Germany during 1868, Karl Alexander von Martius and Carl Graebe were at Berlin, Wislicenus was commencing his lactic acid work at Zürich, Caro was at Heidelberg, Fittig was at Wöhler's laboratory at Göttingen, and Ladenburg was assistant to Bunsen at Heidelberg. (Victor Meyer had just passed his examinations at the latter university at the age of nineteen.) Markownikow and Beilstein were in Russia, where the latter already was hard at work on his "*Handbuch*." Körner, at Palermo, was busily engaged in his classical investigations on orientation.

At the Greenford Green dye works of the firm of Perkin and Sons in England, William Henry Perkin, at the age of thirty, was an accomplished chemist with no less than twelve years of experience in the first synthetic dye plant ever operated. In 1856, on oxidizing crude aniline, he had discovered for the first time a method of preparing a dyestuff synthetically. Against the advice of his teacher Hofmann, who was then at the Royal College of Chemistry in London, Perkin resigned his assistantship at the college, set up a factory, and was soon manufacturing his *mauve* on a commercial scale. The new dye, which was the first rival of the naturally occurring products, soon acquired great popularity and it once brought as high a price as the corresponding weight of platinum. Following Perkin's lead, several other factories sprang up in England, as well as a few in Germany and France. Satisfactory methods of distilling coal tar, and of preparing the necessary intermediates were soon developed in England, and the dye producers also had successful alkali and acid industries from which to draw supplies. New processes for the manufacture of mauve were

discovered, and new dyes of the mauve and of other types soon made their appearance. It was a veritable wonderland of discovery, fame, and fortune.

No small part in the development of the English dyestuff industry was that played by a small group of German chemists. Hofmann's discoveries in the field of the aromatic amines formed the basis upon which the industry had been founded, and most of the important English chemists had received their training in Hofmann's laboratory. Though he had not encouraged the attempts to commercialize Perkin's first discovery, he soon gave his full support to the new industry and played a leading part in the scientific study of the new products. It was through his influence that his countrymen, Martius and Griess, were in England at this time. Heinrich Caro, after a few years of experience in madder dyeing in Alsace, was attracted by the thrilling discoveries in England and he secured a position with the firm of Roberts and Dale at Manchester in 1859. His dreams of sharing in the romantic successes were soon realized, for he proved to have a remarkable faculty for unearthing new reactions and compounds. Like Perkin, Martius, and Griess, he kept in close touch with Hofmann's laboratory and investigated the purely scientific side of the technical problems as fully as time permitted. Among his many achievements in this early period, Caro discovered a new method of making mauve and, with Martius, he introduced Manchester Brown and Martius Yellow. The list of the other dyes which appeared on the market at this time includes Crysaniline, Rosolic Acid, Spirit Blue, Paeonin, Azulin, Regina Violet, Methyl Rosaniline, Aniline Green, Aniline Black, and Diphenylamine Blue.

All of these substances had been discovered without any reference to a theory of color and without any knowledge of the structures of the dyestuffs which occur in nature. The structures of the synthetic products were unknown and, until the benzene problem had been solved, unknowable. Thus about ten years after Perkin's initial discovery of mauve the progress of the new industry began to slacken perceptibly. Discoveries based largely upon chance or accident could not continue indefinitely. The leaders in the early, feverish advances realized that the further development of the field had to wait for pure science to catch up with the empirical discoveries of the industry. The announcement of the Kekulé theory in 1865 was the signal that the time had come for a change, for it now seemed possible to work out the structures of the dyes in the light of the new conceptions of the nature of aromatic compounds. Rational plans for the advancement of the industry could then be made. Thus Hofmann left the scene of the greatest activity in the dyestuff field and returned to Germany in 1865. Martius followed his former teacher; Caro, bent on purely scientific investigations at Heidelberg, returned in 1866. This young but famous technologist, however, could not long remain out of contact with the industry and, three years later, Caro became co-director with

Glaser of the dye laboratory of the Badische Anilin und Soda Fabrik at Ludwigshafen. This young company had been formed in 1865. In that year it employed thirty workmen; in 1914 the number had mounted to over ten thousand.

This, then, was the state of affairs when the investigation of alizarin was undertaken by Graebe and Liebermann in 1868. The stage could not have been set more appropriately for the synthesis and the determination of the structure of one of the most beautiful and important of natural dyes. The need for such an achievement was felt by both the industry and the science, and the theoretical guide to the accomplishment had just become available.

No actor was better suited to play the leading rôle than Carl Graebe. A student of Kolbe, he had spent brief periods in the laboratories of Bunsen and of Erlenmeyer, and he had worked for a year in the Höchster Farbwerke laboratory of the firm of Meister Lucius u. Co. The problem of searching for new dyestuffs interested him, but a case of poisoning by methyl iodide caused him to break this industrial connection. In 1865 he accepted a position as assistant to Baeyer in the *Gewerbe-Akademie* at a salary of three hundred dollars. His relationships here were very pleasant and he found in Baeyer, who was his senior by six years, a warm friend and a stimulating leader. He was introduced to Kekulé one day while carrying out a combustion, and he had an opportunity to talk with this personality for several hours. Writing to his parents, Graebe described Kekulé as

> ....an exceptionally amiable person, which pleased me all the more because I hardly expected that Kekulé, who is one of the most influential chemists of the time, would bother much about us young people. Kekulé spoke about everything, about himself, his relationships, his work, as though we had been old friends.... That Kekulé knows what he is, is often noticeable in the course of the conversation, but this never appears in an unpleasant or arrogant manner.

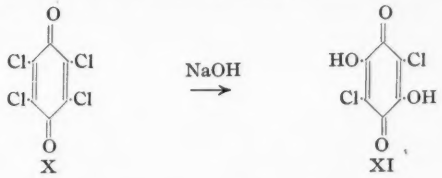
In his first attempts to apply the doctrines of his new-found friend, Graebe became interested in the quinones. These fascinating substances had formed a perplexing problem and even Kekulé had been so far in error concerning their constitution that he had regarded them as open-chain compounds. His formula for quinone was:

$$O{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH{=}O.$$

Working with chloranil rather than quinone, on account of the great expense of the latter compound, Graebe was impressed by the fact that the quinone is easily converted by reduction into a truly aromatic compound. It was hard to believe that ring-closure took place in the course of this simple reaction, and it seemed more probable that both the quinone and the hydroquinone contain the benzene hexagon. He was able to prove this by the conversion of chloranil into hexachlorobenzene. In reasoning about

the positions of the oxygen atoms, he took it as a fact that neither resorcinol nor catechol are capable of yielding quinones on oxidation, in the manner characteristic of hydroquinone. The first proposition is still regarded as being true, but it is now known that the oxidation of catechol to *o*-benzoquinone may be accomplished by carefully maintaining a very special set of conditions. It is thus perfectly clear why hydroquinone was considered to be unique. Graebe reasoned that if only one of the three dihydroxybenzenes yields a quinone, this must be due to some special structure of the compound in question. It was reasonable to infer that the special structure was that in which the two hydroxyls are in close proximity, and he thus regarded hydroquinone as the *ortho* derivative, and for quinone he wrote the formula:

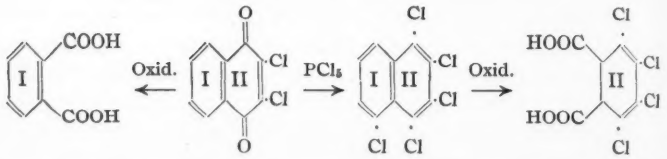
While his formula was wrong in two respects, Graebe's theoretical conceptions, as well as the excellent experimental work contained in his 65-page *Annalen* paper, represent great advances in the knowledge of this interesting group of compounds. This work was of great assistance in solving the alizarin problem, and it is important to notice that Graebe had become familiar in this early work with the fact that the quinones are easily reduced, that chloranil, X, may be converted into chloranilic acid, XI, by the action of aqueous alkali, that hydroxyquinones form highly colored



X XI

solutions in alkali, and that their reduction products are readily oxidized in alkaline solution by the air.

With this experience, Graebe turned to the chemistry of naphthalene and he soon became convinced that Laurent's chloro-naphthalenic acid and its supposed chloride (2,3-dichloro-1,4-naphthoquinone), as well as the supposed isomer of alizarin, which had been discovered by Martius and Griess were all quinones of the naphthalene group, or naphthoquinones. His only error lay in regarding the parent substance of all of these compounds as an *ortho* derivative, for he then considered that no other type of quinone was possible. A very valuable part of this naphthoquinone work was to prove for the first time that naphthalene contains two benzene rings. His proof is indicated by the following reactions:



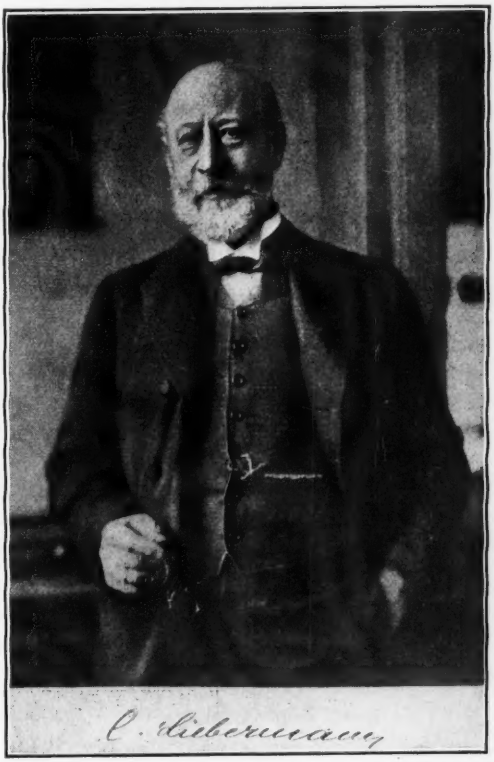
That this work led Graebe directly to the alizarin problem is obvious. Alizarin was generally regarded as an isomer of the substance which Graebe had shown to be an hydroxy-naphthoquinone, and a study of the dyestuff was thus the next logical step in his quinone work.

Graebe's collaborator, Carl Liebermann, was one year younger and had had less experience in scientific work. A *Burschenschafter* active in the *Allemania* at Heidelberg, Liebermann had taken his degree at the *Gewerbe-Akademie* in 1863 and then turned to industrial work in accordance with the wishes of his father, the *Geheimer Kommerzienrat* Benjamin Liebermann, who owned a prosperous cotton mill near Berlin. The young chemist was sent to a large dye and print works in Alsace for training as a colorist. Here he became familiar with the process of dyeing with madder, and with the method of preparing extracts of the dyestuffs which it contains, but he soon became dissatisfied with this occupation. After the exact methods practiced in Baeyer's laboratory it was disappointing to work with a substance of such a variable nature as madder. Samples differed considerably in composition and in the concentration of the active matter, and the control was not exact. A common method of testing consisted in chewing a sample of madder. Sand was detected in an obviously unpleasant manner, and the color of the sputum afforded an indication of the tinctorial qualities. Regarding his attitude, Liebermann says:

> One day I saw at a church festival a group of old peasant women wearing madder-colored scarfs from our factory. These scarfs had cost my friends, the colorists, their positions because the red had turned out a little too bluish. It became clear to me that I could not contemplate a life-work spent in attention to such details.

Thus Liebermann gave up the idea of industrial work and in 1867 returned to the laboratory of the esteemed Baeyer. Here he was to devote fifty years of his life to active scientific work. In looking for a problem it was natural that he should think of working on madder, or rather the substance alizarin which he had learned to extract from it. Perhaps through a knowledge of the chemistry of alizarin it would be possible to introduce really scientific methods into Turkey Red dyeing.

Liebermann soon found a close friend in Graebe, the young assistant, and it is recorded that each confided in the other the intention of working on the dyestuff when they were walking home part of the way together. The decision to collaborate followed and, after securing the material for



their experiments, they started active work on a Friday, February 21, 1868. Friday, Saturday, Sunday, and Monday were spent in energetic work, and by 7 o'clock on Monday evening they had advanced so far that they were able to communicate an important result at the meeting of the *Chemische Gesellschaft* which took place at seven-thirty. They had applied a reaction which Baeyer had discovered in the previous year in the course of his indigo work. He had succeeded in reducing indigo to oxindol by ordinary methods, but the elimination of the last atom of oxygen required a more vigorous reducing agent. Baeyer had tried passing the vapor of oxindol over heated zinc dust and had discovered indol, the mother substance of indigo. The reaction, which was also found to afford a simple means of converting phenol into benzene, was applied by Graebe and Liebermann to the oxygen-containing alizarin. Instead of naphthalene, which would have been expected on the basis of the current idea of the structure of the dyestuff, a hydrocarbon was obtained which was soon identified as anthracene. A careful review of the published analyses of alizarin revealed the fact that the best results indicated the formula $C_{14}H_8O_4$, and the combined information definitely classed the substance as a derivative of anthracene rather than of naphthalene. This accounted for the failure of all previous attempts to prepare the dye, for they had all started with the latter hydrocarbon.

Some impression of the local interest in the discovery and of the excitement of the event is furnished by a letter from Graebe to his parents, in which he speaks of the celebration of his twenty-seventh birthday on the

24th, and of the report which he made to the *Chemische Gesellschaft* on that day:

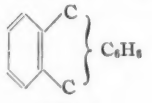
> Unprepared as I was, I spoke briefly about the most important results. That was the first celebration. The second was at a dinner at Baeyer's which was just for close friends. When we went in to dinner I found at my place a wreath of madder blossoms. Baeyer proposed a toast to Dr. Liebermann, whose birthday was on the 23rd, to myself, and to our work. I made a reply, and I do not think I am mistaken in believing that I spoke very well.

Even the great Bunsen was impressed by the work of the two young men, for he mentioned it in a letter to Kolbe.

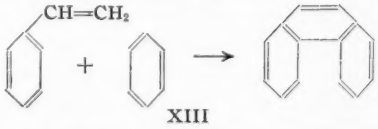
Anthracene had been isolated from coal tar, and Graebe and Liebermann at once speculated on the possibility of preparing the dyestuff from this hydrocarbon. The substance was not easy to obtain, however, and the two investigators were very fortunate in securing about 500 grams of the material from Martius, who purchased it for them in England.

While their attempts at a synthesis were under way, Graebe and Liebermann were also engaged in a study of other substances similar to alizarin. Applying Baeyer's reaction, they were able to show that several other substances of the madder and of the rhubarb group are derivatives of anthracene. They also studied the bromination, sulfonation, and hydrogenation of this hydrocarbon, and they published a paper on the relationship between molecular constitution and color. The frequent occurrence of the quinone grouping, and of other unsaturated groupings, in colored compounds was stressed for the first time.

When they undertook a synthesis, Graebe and Liebermann were still far from a complete knowledge of the structure of alizarin. They knew only that the carbon skeleton was the same as that of anthracene, but the structure of this hydrocarbon had not been established. Graebe and Liebermann, in fact, were the first to discuss the problem of its structure. Their own observation that alizarin is derived from anthracene, coupled with the fact that the dyestuff yields phthalic acid on oxidation, furnished evidence that eight of the carbon atoms are arranged as in XII, for Graebe



XII

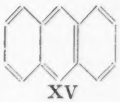


XIII

already had pointed out that the unique ability of phthalic acid to form an anhydride is strong evidence for the *ortho* structure of this acid. On the basis of the Kekulé theory, the above facts, together with the empirical formula, indicated that anthracene must contain three benzene rings joined in either a linear or an angular manner. There was thus a choice between the present formula for anthracene and the formula which we assign to

phenanthrene, for the latter hydrocarbon was still unknown. The angular formula was preferred by Graebe and Liebermann partly because it seemed to explain more easily Berthelot's synthesis of anthracene from styrene and benzene, by passing the vapors of the compounds through a hot tube, which they represented as in XIII, and partly because the arrangement of bonds in the para-bond formula, XIV, with which they represented the linear structure, seemed to them to indicate a more unusual set of properties

XIV



XV

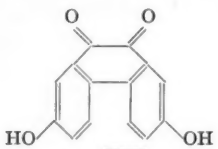
than were found in the hydrocarbon. They were here treading on very uncertain ground, but their error of intuition is easily understood when it is recalled that they were struggling with a problem which is not yet completely solved. Anthracene has a linear structure, but the evidence regarding the distribution of bonds has not yet distinguished definitely between XIV and XV.

Graebe's knowledge of quinones soon led to the recognition that alizarin has all of the properties characteristic of such substances. The color reactions, the ease of reduction, and the air-oxidation of the reduction product furnished convincing evidence that alizarin was a quinone. It must be derived from the quinone of anthracene. Anthraquinone had been prepared by several investigators who had styled it variously as "para-naphthalose," "anthraceneuse," "oxanthracene," and "oxyphoten," but no one had attempted to assign it a formula. It was found by Graebe and Liebermann to have the properties of a quinone, and they gave it the present name. The question as to whether it is a terminal ring or the central ring which is quinonoid was decided in an ingenious, if not an altogether logical, way. Naphthalene is oxidized to a quinone more easily than is benzene, they said, and naphthalene has a greater accumulation of carbon atoms. Since anthracene is oxidized with still greater ease, the oxidation must attack the point where the accumulation of carbons is the greatest, and that is in the central ring.*

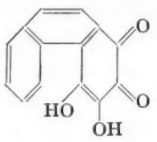
* This rather vaguely expressed idea may be developed into an entirely sound argument. When it is a question of a substitution at the β-position, naphthalene does not appear to be any more reactive than benzene; but the α-position is attacked with particular ease. A parallel is found in the behavior of ethyl benzene. The α-position is easily substituted by, say, chlorine, but there is no special reactivity at the β-position. It is reasonable to say that in each case the unsaturated phenyl group activates the hydrogen attached to the α-carbon atom. Since anthracene is more easily oxidized than naphthalene, it is logical to infer that the points of attack are the 9,10- or meso carbon atoms, for both of these carbons are in a position to be activated by phenyl groups. We thus attribute the effect to an "activation by adjacent phenyl groups," which corresponds to an "accumulation of carbon atoms."

This conclusion seemed to be supported by the fact that anthraquinone is a very stable substance and differs in this respect from compounds such as hydroxy-naphthoquinone, in which the quinonoid ring occupies a terminal position. Thus Graebe and Liebermann were of the opinion that anthraquinone is represented by the formula which we now use for phenanthrenequinone.

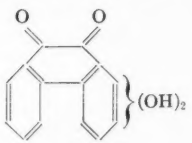
Alizarin contains two more oxygen atoms than anthraquinone and it is a weakly acidic substance. These facts were well explained by regarding alizarin as a dihydroxy-anthraquinone. Since the dyestuff yields phthalic acid on oxidation, rather than a naphthalene dicarboxylic acid or a product derived from hydroxy-phthalic acid, formulas such as XVI and XVII were ruled out and alizarin probably corresponded to the formula: $C_6H_4(CO)_2$-$C_6H_2(OH)_2$. They thus believed that alizarin is what we would call 1,2-,



XVI



XVII



XVIII

1,3-, 1,4-, 2,3-, or 3,4-dihydroxyphenanthrenequinone, XVIII. On the basis of the facts actually available, it was also possible that alizarin and anthraquinone had a linear structure. If we accept their correct, if not altogether soundly founded, hypothesis that the two oxygen atoms of anthraquinone are in the central nucleus, it is found that they were justified in considering that alizarin might have any one of nine formulas.

It is clear that when they undertook to prepare alizarin by synthesis they were taking a one-to-nine chance that their dihydroxyquinone, provided they were able to obtain one, would have the correct structure. Without being aware of the extent of the odds which were against them they soon attempted this synthesis. The reasoning upon which their method was based contains two fallacies. Alizarin, they argued, is a hydroxyquinone and so is dichloro-dihydroxy-quinone (chloranilic acid), as well as chloro-hydroxy-naphthoquinone (chloro-naphthalenic acid). The latter substances are obtained by the action of aqueous alkali on tetrachloro-quinone and dichloro-naphthoquinone, respectively. Therefore, they said, dibromo-anthraquinone must yield a dihydroxy-anthraquinone on similar treatment. Knowing as we do the correct structures and the properties of all of the compounds concerned, it is obvious that they were expecting too much. It is impossible, by the action of aqueous alkali, to replace by hydroxyls *both* chlorine atoms of dichloro-naphthoquinone or *all* of the halogen atoms of chloranil. This is the first fallacy. The second consists in assuming that halogen atoms attached to a benzene ring would

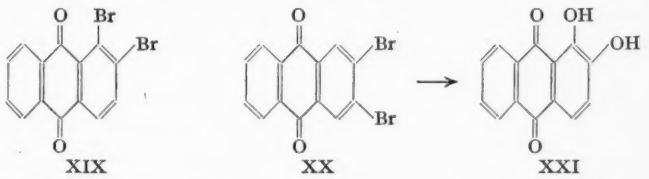
be replaced with the same ease as halogens in a quinonoid nucleus. They were aware of the fact that a hydroxyl group is very much more acidic when in a quinonoid nucleus than when it is in a benzene ring, and they should have seen that a halogen atom would exhibit similar differences in reactivity. The reaction which they proposed to employ was one for which there was no parallel. A benzene halide had not yet been converted into a phenol. This reaction had been found useful and suitable for industrial application only within the last few years.

It is altogether remarkable that Graebe and Liebermann, basing their plans upon reasoning which must be regarded as faulty, and looking for one compound out of a possible nine, actually succeeded in synthesizing alizarin. In 1869 they dibrominated anthraquinone and treated the product with aqueous alkali. No reaction took place at first, but they boiled the solution down and heated the mixture to a high temperature and under these conditions a substance was formed which was found to be identical with natural alizarin. For the first time a naturally occurring and a very beautiful and important dyestuff had been produced synthetically. There are nine dihydroxy-anthraquinones, but only a single one of these is a dyestuff. They obtained that compound.

The discovery was widely acclaimed and the names of Graebe and Liebermann were by-words. Accounts of the work appeared in the daily papers and the young chemists received the universal praise of their colleagues. They were not slow in realizing the importance of their own discovery. When they published their results, Graebe and Liebermann said:

> We need not point out the importance of our discovery for the madder industry if it is possible to make a technical success. The enormous consumption of madder and the large tracts of fertile soil required for its cultivation clearly bespeak the importance which would be obtained by a new branch of industry based on the artificial preparation of alizarin from a constituent of coal tar.

One of the most remarkable aspects of their synthesis has only come to light in recent years. When the true structure of alizarin became known, it was generally assumed that the dibromo compound which they had employed was the 1,2-derivative, XIX. This was a perfectly reasonable inference. But it has been shown clearly that the compound employed by



XIX XX XXI

Graebe and Liebermann in their first synthesis of alizarin actually has the structure of 2,3-dibromo-anthraquinone, XX. A rearrangement evidently

takes place when this substance is fused with alkali. It is probable that a dibromo-benzoyl-benzoic acid is first formed, that the bromines are then replaced by hydroxyls, and that subsequent ring closure results in the formation of alizarin, XXI. It is very evident that fortune favored the investigations of Graebe and Liebermann to a marked degree. On the other hand, the subsequent careers of each of these investigators has shown that they were exceptional men who adequately merited such exceptional good luck.

The synthesis was reported at a meeting of the *Chemische Gesellschaft* on January 11, 1869, at which time samples of the synthetic material and of dyeings were exhibited. Having secured patents, Graebe and Liebermann considered various plans for the technical application of the discovery and in May a contract was signed with the Badische Anilin und Soda Fabrik calling for a 3% royalty over a period of fifteen years. Caro, a skilled Turkey Red dyer and himself a veteran discoverer of dyes, undertook to work out the technical production of alizarin and Graebe went to Mannheim to assist him. It was soon found, however, that the great expense of bromine and the difficulty in carrying out the bromination and the alkali fusion in the reaction vessels then available rendered the process impractical.

A search for a more suitable method of preparing the dyestuff was commenced without delay. Other methods were available for introducing the hydroxyl group, the oldest being by way of the diazonium salt. This rather lengthy procedure had been used for some time in the technical production of α-naphthol, but a much simpler reaction, which consisted in the alkali fusion of an aromatic sulfonate, had just been discovered in 1867 by Kekulé, by Wurtz, and, in a sealed note deposited earlier, by Dusart. But when Graebe, Liebermann, and Caro attempted to apply this splendid new method the results were discouraging. When they followed the usual procedure for effecting a sulfonation the anthraquinone was recovered unchanged. Compounds of the stability and the resistance to substitution which characterizes anthraquinone were rare, and a moderate temperature and the ordinary concentrated acid were all that had ever been required. Fuming acid had rarely been used in sulfonations, especially in Germany. It was only through an accident in Caro's laboratory that the conditions required for bringing about the sulfonation were discovered. It was known that phenols could be condensed with oxalic acid in the presence of sulfuric acid to give triphenylmethane dyes of the type of rosolic acid. Caro thought that the oxygen-containing anthraquinone might react in some similar fashion, and he had just started to heat a mixture of this substance with oxalic and sulfuric acids when he was called to another room. The flame had not been adjusted and, when he returned, the laboratory was filled with dense fumes and he found that his mixture had boiled down

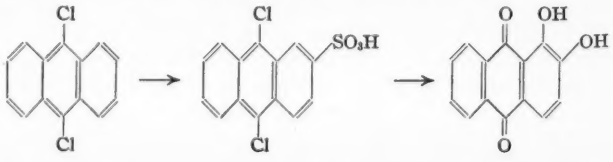
nearly to dryness. On closer examination he found that the anthraquinone, at the high temperature which had resulted from his carelessness, had been sulfonated. It was soon found that the sulfonated anthraquinone may be converted easily into alizarin by fusion with alkali, and a second method of preparing the dyestuff was thus available.

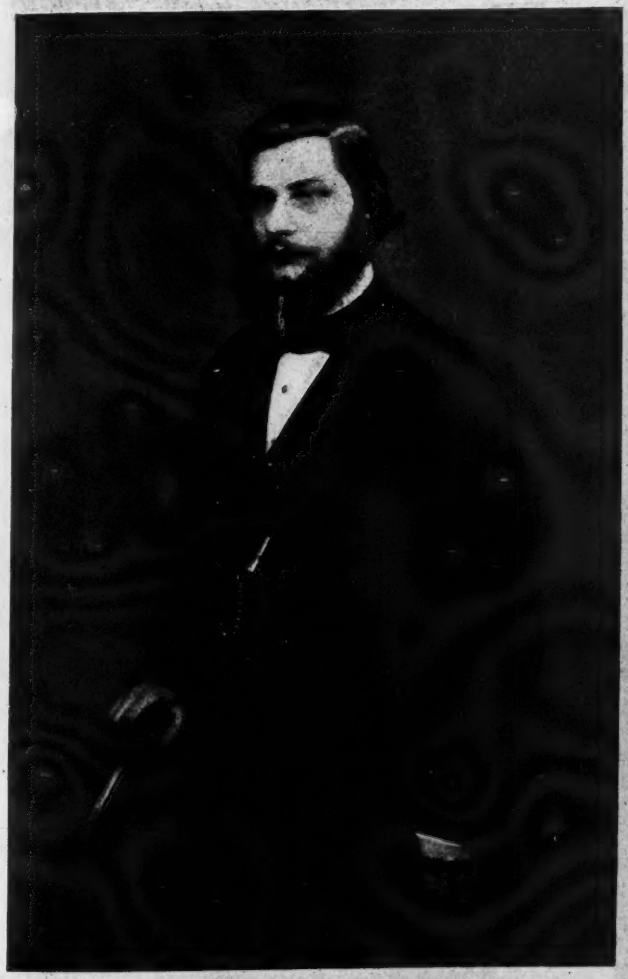
The new process was found to be admirably suited to large-scale production, but a bitter disappointment was in store for the three investigators. In reply to their application for a patent in Prussia, they were informed that, since they had merely substituted one anthraquinone derivative for another, a disulfonate for a dibromo compound, there was not sufficient novelty in the method to entitle them to a second patent. On the other hand, the original patent did not prevent competitors from using the sulfonation method. Thus the Badische Company found itself in the very awkward position of having full patent protection for their unworkable process, but no protection at all for the process which actually worked. The result was that the manufacture of alizarin was undertaken by no less than eight different German firms, and the Badische was perhaps the worst off of all because of the royalty which they had agreed to pay to Graebe and Liebermann.

Better results were expected in England, but the Germans were here

robbed of the full success to which their discoveries entitled them by a remarkable coincidence. The patent application of Caro, Graebe, and Liebermann was sent to England early in June, but there was some delay on account of changes in the wording and the application reached the British patent office on June 25th. Here there was further delay and the application was set aside for several weeks. On June 26th an application covering exactly the same process was filed by Perkin. The Englishman's application was examined at once and Perkin was soon granted a patent. Rather than attempt to restrain the Perkin patent by entering into litigation, Caro, Graebe and Engelhorn, a business director of the Badische firm, went to England to confer with Perkin and an agreement was effected to divide the market.

It is interesting to observe that Perkin's independent discovery was inspired by a perfect series of circumstances. Perkin's first research problem at the Royal College of Chemistry was to prepare an amine of anthracene; this was to be a part of Hofmann's famous amine work. Though he never achieved this end, he learned how to prepare anthracene from coal tar, and he studied the oxidation and chlorination of the hydrocarbon. Thus Perkin was one of the few chemists of the time with any personal experience in the anthracene series. The second circumstance was that the synthesis of natural products appealed to him as a particularly fascinating and valuable type of work. His discovery of mauve was the result of an unsuccessful attempt to synthesize quinine by the oxidation of allyl toluidine. The publication by Graebe and Liebermann of the first alizarin synthesis made a profound impression on Perkin, and this skilled chemist, whose own dye firm was in need of new processes, who had some familiarity with anthracene, and to whom such syntheses appealed strongly, at once set out in search of some means of dispensing with bromine. His process of reasoning, though not recorded, must have been something like this. The use of bromine might be avoided by using the new method of Kekulé, Wurtz, and Dusart, were it not for the difficulty in sulfonating anthraquinone. Perhaps anthracene sulfonates more easily; it might be sulfonated and then oxidized to an anthraquinone. This is the case, but the reaction appears to be quite complicated. He was thus led to try a derivative of anthracene which he had prepared in Hofmann's laboratory. 9,10-Dichloro-anthracene was found to sulfonate readily, and it was not even necessary to oxidize the product to a quinone, for the sulfonated dichloro-anthracene yielded alizarin when fused with alkali:

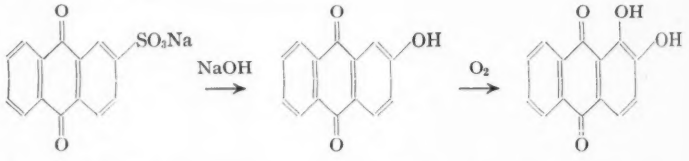




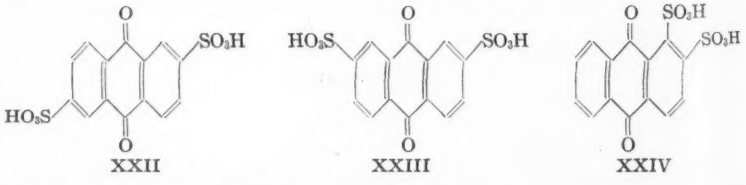
W. H. Perkin
at the age of 22. (1860)

Perkin subsequently found the means of sulfonating anthraquinone itself, so that he was in possession of two satisfactory processes for manufacturing alizarin.

It is well known that the reaction by which alizarin is formed in the successful industrial processes is not a simple one. It was at first assumed that a disulfonate of anthraquinone was responsible for the production of the dye, but when attempts were made to carry out the fusion in closed vessels the supposed disulfonate yielded a considerable amount of 2-hydroxy-anthraquinone. This reaction, as well as analyses of the sulfonate, soon established the fact that it is the β-monosulfonate which produces alizarin and that the replacement of the sulfonate group is followed by an oxidation by atmospheric oxygen:



This unusual reaction could not have been predicted. In fact, if the young discoverers had known the true structure of alizarin and the rules of substitution they probably would not have made the discovery, at least not in so direct a manner. The first sulfonic acid group enters the β-position because this is *meta* to an unsaturated carbonyl group. The second substituent surely would not enter a position which is *ortho* to two *meta*-directing groups, but would be thrown into one or the other of the two β-positions of the second ring, as in XXII and XXIII.



This is what actually happens. Thus it would have been folly to attempt to make XXIV by disulfonation with a view of converting it into alizarin.

The structure of alizarin became fully established a few years after the synthesis had been achieved. The correct position of the three rings of anthracene became known through the work of Van Dorp in Liebermann's laboratory, while the discovery by Baeyer and Caro of the hydroxy-anthraquinone synthesis from phthalic anhydride and phenols led to a proof of the positions of the hydroxyl groups in alizarin. This work will not be described, nor will any mention be made of the many amazing dis-

coveries which followed in the wake of the alizarin work and which rank among the most brilliant achievements of the science.

The most immediate effect of the alizarin synthesis was on the young German dyestuff industry. The sulfonation process, unprotected by patents, was studied with great energy in the laboratories of several independent firms, and the keen competition in the field accounts for the surprising speed with which the details of the technical process were worked out. Means were found for obtaining anthracene in quantity, and the oxidation to anthraquinone was accomplished by the use of dichromate in dilute acid suspension. The demand for fuming sulfuric acid, which gave less of the undesirable disulfonates than when concentrated acid was used, eventually led to the discovery of the contact process (1875). The practice of carrying out the alkali fusion in the open (at first in silver vessels) was soon abandoned in favor of Koch's process, according to which the mixture is fused in an autoclave under pressure and the oxidation is brought about by the addition of potassium chlorate, or another oxidizing agent. So rapid was the progress that by January, 1871, the technical production of the dyestuff was in full swing. Thus alizarin from coal tar was on the market exactly two years after the first synthesis had been reported. The product was of excellent quality, and much more easily applied than madder. The color could be varied from red to bluish or yellowish red by making slight changes in the process. When pure anthraquinone-2-sulfonate was employed and the fusion carried out with a minimum amount of chlorate, a very pure alizarin was obtained which furnished a bluish red dyeing. On fusion at a higher temperature, and with more chlorate, a certain amount of the alizarin was oxidized to purpurin and the dyeing was redder. If the sulfonation was carried somewhat beyond the point of monosulfonation, a product containing the 2,6- and the 2,7-disulfonates resulted. Each of these acids on fusion becomes hydroxylated in the α-position during the process, and thus the alizarin which is prepared from a mixture of the mono- and disulfonates contains the trihydroxyanthraquinones: flavopurpurin (1,2,6), which is yellowish, and anthrapurpurin (1,2,7), which is reddish. Some variety was thus possible. Excellent yields were obtained. It is reported that in 1877 the average yield from 100 parts of anthracene was 100–105 parts of alizarin, or about 79% of the theoretical figure.

Madder could not compete with the manufactured material in price, ease of application or quality and the cultivation of the plant had to be given up entirely within a few years. An industry worth about sixteen million dollars per year was wiped out completely, and this source of revenue was largely transferred from France to Germany. Due to the active competition between the various firms, and to the technical improvements, the price of alizarin dropped steadily until it was finally fixed in

1881 at a figure which was about one-sixth of that ten years earlier. It is estimated that the cost of dyeing with Turkey Red dropped to one-twentieth of its former figure. The consumption of the dyestuff increased regularly until about 1900, when the annual production of alizarin (dry) amounted to about two million kilograms. With the changes in the chemical industry resulting from the war, and with the introduction of cheaper dyes, the production of alizarin has fallen off considerably.

If alizarin has finally relinquished its position as one of the dyes of greatest commercial importance, the manufacture of this substance will always be remembered as one of the chief factors in the development in Germany of a chemical industry which has dominated the field. For the successful operation of the alizarin factories, acids, alkalies, and chlorates were required in large quantities. Considerable coal tar had to be distilled in order to furnish the anthracene and uses had to be found for all of the other coal-tar crudes. Thus all branches of the industry were given a great stimulus by the production of a single dye. The English dyestuff industry, founded upon a discovery of a youth of eighteen, had developed more rapidly at first, but soon after 1870 it was overshadowed by the remarkable advances in Germany, particularly by three great firms: the Badische Anilin und Soda Fabrik, the Höchster Farbwerke vorm. Meister Lucius und Brüning, and the Elberfelder Farbwerke vorm. Fr. Bayer.

The two men who were responsible for these striking results received very little monetary compensation for their discoveries. Graebe lost his modest fortune during the period of inflation and died in 1920 a penniless old man of eighty. Neither collaborator could be persuaded to go into the industry, where he might have capitalized the early successes. In Graebe's case the choice was made largely because of the pleasure which he derived from delivering lectures.

Both Graebe and Liebermann acquired considerable fame as teachers and investigators, particularly in the chemistry of the quinones and of the more highly condensed hydrocarbons. Houben's "*Das Anthracen und die Anthrachinone*" contains no less than 382 references to the researches of these two men. In each of forty-seven consecutive years, the *Berichte* contains one or more papers under the name of Carl Liebermann. These facts give a rough idea of the extent of the contributions which followed the famous work on alizarin. One further pleasant fact which may be recorded is that the great friendship which had existed between the two young collaborators was maintained throughout all of the subsequent years when Liebermann remained at Berlin while Graebe moved to Leipzig, to Königsberg, to Geneva for a period of 28 years, and finally to Frankfort and retirement. In 1911 the president of the *Deutsche Chemische Gesellschaft* sent to a former president of the society a letter of congratulation on the occasion of the latter's seventieth birthday. The recipient of the letter

was Carl Graebe. He addressed his reply, in formal fashion, to the *Herr Geheimer Regierungsrat* Prof. Dr. Carl Liebermann, but he employed the intimate form of speech in expressing his thanks for the many compliments of his *Lieber Freund.*

Bibliographical Note

References to the original literature concerning the history of alizarin are given in the monographs, references 1–5, listed below. Much additional information for the present account was taken from the biographies, references 6–9. The remaining references are to papers which have not been discussed in most of the earlier accounts.

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(*10*) C. LIEBERMANN, "Glückwünsche an Hrn. C. Graebe," *Ber.*, **44**, 551 (9111).

(*11*) C. GRAEBE, "Ueber Naphthalin," *ibid.*, **1**, 36 (1868).

(*12*) C. GRAEBE and C. LIEBERMANN, "Ueber Farbstoffe aus der Anthracengruppe," *ibid.*, **1**, 104 (1868); "Ueber Zusammenhang zwischen Molekularkonstitution und Farbe bei Organische Verbindungen," *ibid.*, p. 106; "Ueber Anthracenderivate," *ibid.*, p. 186; "Ueber Anthracen und Alizarin," *Ann. Spl.*, **7**, 257 (1870).

Turning Sawdust to Sugar. Dr. Friederich Bergius is the German chemist famous for turning coal into gasoline. He has also turned sawdust to sugar, for cattle feeding.

Dried sawdust is leached with concentrated hydrochloric acid, according to a description recently given by Bergius himself, in New York, reported in *Food Industries*. This produces a sirup of high acidity. The acid is removed by mixing the sirup with hot oil, in a vacuum, when it becomes gas, and is absorbed in water. The sirup is then evaporated to a dry product, which is a food for animals.

The exact identity of the sugars has not yet been determined, but they are digestible carbohydrates which animals convert into corn sugar. They can be refined for human consumption. Sawdust yields sixty-five per cent of its substance in these sugars.

It has taken Dr. Bergius at least ten years to perfect the technical process, although the chemical studies, started in 1913, were completed in three years.—*Chemistry & You*

WORLD CONDITIONS AS TO CHEMICAL PLANT FOODS*

C. C. CONCANNON, CHEMICAL DIVISION, DEPARTMENT OF COMMERCE, WASHINGTON, D. C.

The fertilizer industry was founded primarily to serve as a salvage outlet for the waste products of other industries. From a lowly start the industry has grown to be the giant of the chemical industry. It now assembles materials from the atmosphere, the animal, mineral, and vegetable kingdoms—processes, compounds, and mixes them—and in a short season of about ten weeks distributes the bulk of its 8,000,000 tons of products.

Unlike the automobile, motion picture, and certain other industries that are referred to as American developments, the fertilizer industry has always been international in its scope, not only insofar as it involves the transportation of raw materials from one country to another, but also as regards the transfer of manufacturing processes, and indirectly, but of paramount importance, as a contributing factor in making available export surpluses of agricultural crops. To illustrate, we have imported Chilean nitrate of soda and European potash since their value as fertilizers became known; we imported certain methods of manufacturing superphosphate and fixed atmospheric nitrogen; and fertilizers make it possible for cotton to be our leading agricultural export.

It is hardly necessary to delve deeply into historical records to establish the relation of international developments to the domestic fertilizer industry, and yet contact with the rest of the world is immediately apparent and it at times becomes equally obvious that any episode or change occurring within the sphere of influence of the plant food world has a very real and ofttimes a direct bearing upon conditions affecting American producers of plant food, an effect which is in turn passed on to the agricultural interests of the country.

The manufacture of fertilizers, or as these products are frequently termed today, "plant foods," has been an increasingly important phase of commerce and industry for many years. It is within the past decade or two, however, that great changes have been experienced and as a preamble to further consideration let us look back as far as 1909 and review a few of the changes of the last twenty years.

A cornerstone for the atmospheric nitrogen industry was laid in 1909 when Professor Haber of Germany patented the results of his experiments in the field of direct ammonia synthesis. Today the direct synthetic ammonia industry is in a position to supply the world demand for commercial nitrogen. In the same year the cyanamide plant at Niagara Falls, Ontario, commenced operations, thus making available to American agriculture its first important supply of atmospheric nitrogen. In the last two decades our coal nitrogen production in the form of ammonium sulfate has grown

* An address delivered at the annual banquet of the National Fertilizer Association, Colorado Springs, Colorado, June 12, 1930.

from 120,000 to over 800,000 tons, becoming our present major source of supply, a position long held by Chile.

Pyrites of foreign origin accounted for a large percentage of our 1909 sulfuric acid production. Our first important sulfur mine, located in Louisiana, only commenced shipments in 1903, and our total production in 1909 was under 300,000 tons, but today much of our sulfuric acid essential in the manufacture of superphosphates is produced from brimstone instead of pyrites and in the production of sulfur the United States leads the world by a large margin.

In 1909 there was no domestic potash production and we paid ocean freight, other foreign shipping expenses, domestic handling and transportation charges on the very lowest grades of German salts. Low-grade kainite, recently discontinued as an important item in favor of higher analysis salts, constituted the bulk of the 350,000 tons of kainite and kieserite imported in 1909.

Low-analysis kainite is not the only material to pass out of the fertilizer picture. In 1909 organic ammoniates, such as cottonseed meal, animal and fish by-products, found their principal outlet as fertilizer. Today these materials are used chiefly for direct feeding of live stock. A study of materials available for mixtures at present compared with those of 1909 would indicate that the plant food content of the present production of 8,000,000 tons of finished fertilizers is exceedingly higher than was contained in the 5,600,000 tons made in 1909. If the increase in total tonnage output during the past twenty years has been disappointing, there is consolation in the fact that the quantities of actual plant food delivered to the farmer have shown a healthy gain.

Many other significant developments of the past two decades could be mentioned and it is reasonable to suppose that the next twenty years will show changes that are now almost impossible of imagination. How will these developments affect the individual fertilizer manufacturer, the mixer, the supplier of materials, the transportation agencies, the banker, the stockholder, and last but not least, the consumer?

The answer to the question will depend upon the individual concerned and the plans he is now making for his future existence. It may not be necessary to follow the lead of one firm in the chemical industry which attempts to forecast commercial developments for the next fifty years, but every firm should have a development program for at least the next three to five or more years. A company with a well-defined program, as well as organizations lacking in this respect, will find the Bureau of Foreign and Domestic Commerce, with its extensive sources of information on conditions at home and abroad, of value in mobilizing and in analyzing the facts that are prerequisite for the successful operation of business.

The Bureau of Foreign and Domestic Commerce, following its reorganiza-

tion by former Secretary of Commerce Hoover, has had a phenomenal growth. This has been due in large measure to the fact that the American business man has found the services rendered by the Bureau of inestimable value and he has insistently demanded from year to year that the government increase the facilities of the Bureau of Foreign and Domestic Commerce. The volume of requests for help of all kinds is now numbered by millions in the course of the year and in order to simplify the contact between the business man and the Bureau a number of branch offices have been set up throughout the principal industrial and commercial centers of the United States. These offices are equipped to render a range and variety of service which must be experienced in order to be fully appreciated.

Mr. Hoover, while Secretary of Commerce, and his successor the present Secretary of Commerce, Mr. Lamont, realized that the American business man should have the very highest type of governmental assistance in matters having to do with foreign trade. The Foreign Commerce Service is now well staffed and a corps of active business promoters and news gatherers in the persons of our commercial attachés and trade commissioners are located in fifty offices of the department at focal points in most of the countries of the world. It was the great ambition of Dr. Klein, while he was Director of the Bureau of Foreign and Domestic Commerce, to build up this foreign service and now Dr. Klein as Assistant Secretary of Commerce and Mr. Cooper, the present director of the Bureau, are ever on the alert to see that the service is maintained at its high degree of efficiency. In order to take care of matters affecting the fertilizer industry among other branches of industry the Chemical Division was established in the Bureau of Foreign and Domestic Commerce. This division fortunately is charged with no regulatory duties but its activities are entirely of a constructive character. Matters having to do with foreign trade promotion and the compilation and dissemination of news are the major function of the Chemical Division. Thus the division comes almost immediately into contact with such items as nitrogen, potash, and phosphates, not only in their relationship to our need for supplies of these materials or from the standpoint of our ability and desire to sell them abroad, but also from the standpoint of general economic and political considerations as, for instance, the national as well as the international cartel.

Fertilizer materials represent an important item in international commerce and it is hardly necessary to state that major developments abroad have their effect on the American industry. With this in mind, a review of the fertilizer material and plant food situation in the principal foreign producing and consuming markets may be of interest.

Nitrogen is a substance which has been known to the chemist for many years but not too well understood by him, particularly in methods of controlling it to the best advantage. Today the words, "nitrogen," "nitrate,"

and other practical synonyms appear prominently in the daily press with sufficient frequency to make them almost household words even though, and this is sometimes too bad, their significance is not generally understood. It is a fact that nitrogen is an essential constituent of the foods required by plants and the economic development of processes for converting the nitrogen of the atmosphere into compounds suitable for use in agriculture assures future supplies of foodstuffs for an ever-increasing world population.

The world production of inorganic nitrogen in 1929 was approximately two and one-half times that of 1913. This achievement of the nitrogen industry is probably the most significant development in the world's chemical industry during the present century.

The success of the pioneer producers of synthetic nitrogen and the apparent desire of every leading nation to be self-sufficient with regard to supplies of nitrogen had led to some overproduction. This has been caused by expansion in several directions. Capacities of the pioneer direct synthetic ammonia plants have been extended and new plants erected. There has been higher recovery of by-product ammonia at coal-distillation plants, increased operating efficiency and expansion of cyanamide plants, and production of nitrate of soda in Chile has outstripped consumption.

The world production of inorganic nitrogen reached 2,250,000 short tons in the year 1928–29, a gain of over 20 per cent in a single year. Much of this output was absorbed by agriculture and industry but there has been some accumulation of world stocks, notably of German synthetic products and Chilean nitrate of soda, these two countries accounting for about 60 per cent of the world production. The nitrogen situation in the United States is somewhat distinct from that of many European countries in that there has been a more orderly development of fixation plants, and, while production has expanded, the United States still imports considerable quantities of nitrogen, chiefly in the form of nitrate of soda from Chile.

As a corollary to world production it is interesting to note world consumption of inorganic nitrogen which in 1928–29 was estimated at 2,050,000 tons, approximately 14 per cent more than that of the previous year. United States and Germany consumed together about 45 per cent of the world supply.

While production may outstrip consumption temporarily there are vast potential markets for nitrogen that await development. Many farmers in certain countries have found it desirable to increase the use of nitrogen for greater crop yields, better products, or as a labor saver by maintaining former production levels with less acreage. In the face of rapidly increasing production throughout the world it is but natural that there should arise a desire on the part of some to control and limit production and a step in this direction was the recent international conference of producers in Paris.

Representatives of the Chilean Government, the British Imperial Chemical Industries, and the German I. G. Farbenindustrie met in Paris on April 28th with the apparent purpose of reaching an international nitrogen accord. The meetings were private and no communication was made to the press concerning the results of the conference. Although it is said that the objects for which the meetings were called were not attained, it would probably be a mistake to believe that the various representatives returned to their respective countries without any result. It was the thought of the conference that overproduction makes it necessary to all concerned that a method be reached for arriving at an international production quota satisfactory to the large producing countries and corresponding approximately to current world demands. Though the recent Paris nitrogen conference has adjourned it is expected that it will reconvene and that another attempt will be made at a later date to arrive at some sort of understanding which will control the nitrogen situation throughout the world. If this idea ever culminates, and there are those who are optimistic as well as those who are pessimistic about the possibility of bringing so many divergent interests into line, there will be set up an international accord which will probably be the world's greatest international cartel.

The futile attempts made some months ago to arrive at an understanding between the Anglo-German-Chilean interests and the Franco-Belgian nitrogen interests clearly showed the difficulties attending any attempt at establishing a friendly working arrangement in this field. Both France and Belgium are among those countries which, for reasons of national defense, since nitrogen is essential for the manufacture of high explosives in war time, decline to consider any and every proposition tending toward limitation of their nitrogen production.

It has been rumored in Paris that the I. G. Farbenindustrie, or the German Chemical Trust as it is frequently called, and the Imperial Chemical Industries of Great Britain working together do not control a sufficiently large percentage of the world's nitrogen production to impose their views on the other producing countries, and furthermore, the position of the I. G. Farbenindustrie, the world's greatest single producer of atmospheric nitrogen, is not the dominating one that it has been heretofore. The I. G. has been facing for some time past the threat of keen competition on the part of the Ruhr industrialists who are able and seem bound to produce increasing amounts of nitrogen at prices which are reported to be under the cost of production possible in the great plants of the I. G. developed years ago under war time conditions. True, an agreement has been entered into between these two groups, and the German Nitrogen Syndicate thus controlling the sale of nitrogen produced in Germany has recently been prolonged for a period of seven years, effective July 1, 1930. This syndicate will include about 98 per cent of the entire German nitrogen production, total sales last

year being approximately 850,000 short tons, and it is easy to see that while this organization in itself may not be a perfect set-up, it, none the less, presents a powerful front to the rest of the world.

In our study of the cartel movement we have found that the ground work must be carefully laid before projects of this kind can even hope to succeed. Small units with common interests must first be fused and these must later be merged with other groups to the end that the great community of interests which is the cartel may come into being.

Calcium cyanamide is one of the oldest forms in which atmospheric nitrogen may be fixed. As a part of all these nitrogen developments, a European calcium cyanamide syndicate was formed on May 3, 1930, under the terms of which sales in each country are confined to the domestic producing establishments. European press reports concerning this International Cyanamide Cartel credit the German producers with the idea of bringing together the producers of cyanamide in order to study the situation as it is affected by the growing world production of ammonium sulfate and new nitrogenous products, as well as the possible effect of a new International Nitrogen Cartel. The cyanamide cartel is reported as having decided that intensive propaganda will be necessary to increase consumption in order to speed up cyanamide plant operations, which are now working at about 50 per cent capacity, and to this end the producers intend to participate in the expense of such a campaign.

The ground work appears to have been laid fairly well for setting up an international nitrogen agreement which would bring together the producers of so-called natural and synthetic nitrates into one of the most powerful world cartel agreements yet conceived. If this is ever consummated one of the important factors therein must be the Chile nitrate interests which have recently received prominent mention in the press of the world because of the proposed complete amalgamation of all present nitrate interests in Chile into one huge corporation.

The new company known as Compania Salitrera Nacional, called "Cosana" for short, or translated into English, National Nitrate Co., will have a capitalization amounting to about $375,000,000 and will include all the nitrate producers of Chile, among whom 50 per cent of the stock of the new company will be divided, with the Chilean government holding the other 50 per cent, in return for which the government will abolish the export tax on nitrate and will receive in lieu thereof approximately $20,000,000 annual revenue for the first four years. The plans apparently involve the closing down and scrapping of all existing plants except the present Anglo-Chilean (Guggenheim process) plant, the large Lautaro plant under construction, and perhaps other strategically located plants which will be built to operate the Guggenheim process on a large scale. Concentration of the industry in a few modern plants will cut the average production costs and it

is expected in Chile that more favorable prices will lead to an upward trend in consumption of Chile nitrate.

In line with this effort to cut production costs other rationalization undertakings are in view, such as, for example, the exportation of the Chilean product in bulk, thereby eliminating cost of bags and cutting the handling costs in transportation. Several experimental shipments have been made with satisfactory results and the significance of this saving is immediately apparent when one stops to realize that the producers of Chilean nitrate paid $6,300,000 in 1928 for bags in which to ship their product.

The general economic and political effect of this new Chile nitrate set-up is epoch-making. One of its immediate effects is perhaps felt most powerfully by those who have been endeavoring to set up an international nitrogen control. The ability and the desire on the part of Chile to increase production and consumption is not a factor which fits comfortably into any idea which may have for its object world-wide control of production and consumption of nitrogen at a fixed price.

Throughout this discussion references to various forms of monopoly control are readily noticeable; fusions, mergers, cartels—national and international—and various forms and stages of control are evidenced. The Bureau of Foreign and Domestic Commerce has been most assiduous in following up economic developments of this kind and the Chemical Division has been active in studying the effects and the results of this form of concerted effort.

The foreign cartel frequently causes the American business man, at first glance, to worry about competition which he must face and the suggestion is often made that our laws should be changed in order to permit American business to combine in similar fashion. Upon more mature consideration it is realized that action of this kind would be a sign of weakness and would not bring about the desired result. As a matter of fact, statute law in this connection is weaker than economic law, and if there is one thing positive about these monopolies and controls it is that they are not the all-powerful organizations which their originators always hope they will be. The community idea is paramount in Europe and business interests get together to control things. In the United States we have a diametrically imposed economic concept and American individualism and initiative have been and will always continue to be fundamental factors in our business and social progress. As President Hoover has so aptly said in speaking of cartels, "They contain within themselves the seeds of their own dissolution."

Among the fertilizer materials, the place occupied by phosphoric acid derived from phosphate rock cannot be over-emphasized. The United States is blessed with a wealth of raw material in this respect and our plant food manufacturers together with our farmers realize that phosphoric acid,

whether it be in the form of superphosphate or in some other form is essential in the proper cultivation of plant life. Our phosphate industry had its inception several generations ago, the most important mines under development being those in Florida not far from Tampa, and while this industry has been through many vicissitudes, the future status of the industry is unquestionably sound. Exports of phosphate rock have in past years run into large tonnage and amounted to considerable value. This business has recently been diminishing due to competition from African phosphates, but a most encouraging factor in the phosphate trade during 1929–1930 was the exceptional demand of European consumers. Relatively more phosphate is apparently being consumed in Europe. American producers share part of this increased demand and this accounted for the gain of 33 per cent last year in our exports of land pebble to 1,075,000 long tons. There are many hopeful signs and not least of these is the reported successful efforts of processing phosphate rock at the mine, with consequent production of finished products of high unit value. American scientists are working on this problem and their efforts will undoubtedly meet with a great measure of success.

Although phosphate rock is found in many parts of the world, it is the North African phosphates which are having the most important present effect upon the world trade in this commodity. Phosphate rock is a leading item in the trade of Tunisia, Morocco, and Algeria, and so far as Morocco is concerned, it is practically a governmental monopoly, carried on by the French government and with considerable success within the past few years. Heavy shipments of African phosphates during 1929, amounting to over 3,000,000 metric tons from Tunisia, 1,600,000 tons from Morocco, and approximately 900,000 tons from Algeria, led to a dearth of supplies in 1930, with stocks at the mines and in the ports reduced to such a minimum that in many cases vessels were obliged to wait for cargoes. Normal conditions are now being gradually re-established. Even in this field, the cartel idea is in effect and it is reported that the long-desired agreement between the Tunisian, Algerian, and Moroccan phosphate mines has been realized as to price, although not as to quantities, but it is obvious that the new price agreement may be considered a step toward a general accord embracing the regulation of production as well.

Potash, a member of the triumvirate of essential materials necessary in plant food, has been supplied to the world in years past largely from German sources. Today, 80 per cent of the American consumption is imported from German and French sources but the 20 per cent of domestic production is quite likely to be increased during the current year from brines at Searles Lake, California, and by mining polyhalite in New Mexico. This domestic production will tend to develop a larger consumption in the United States in new regions, due to the location of the producing plants and the neces-

sity for confining sales to markets that can be economically served in competition with the European sources.

During 1929 the United States imported 870,000 short tons of fertilizer potash salts, having an active (K_2O) content of 300,000 tons. Domestic production amounted to 62,000 tons of potash (K_2O).

Conditions attending potash developments in various countries of the world are most interesting and these developments are of the greatest importance from the standpoint of international politics and economics. To fully appreciate the significance of this last statement we have but to realize that the Franco-German potash accord is the first commercial agreement which was entered into between France and Germany after the war and this international relationship established through potash is the keystone in the arch of subsequent Franco-German trade agreements. The controlling position of France and Germany, acting as a unit in world potash production, has not been changed by recent activities in Russia, Poland, Spain, Palestine, and the United States, where efforts are being made to develop existing potash resources. Much scientific work is being done not only in the field of potash by-products utilization but also in the field of more effective use of potash itself. Most of this work is being done in Germany and in this latter respect it is interesting to note that the use of potash as a carrier for synthetic nitrogen has been developed on a large scale by the Wintershall interests at prices which permit its use in fertilizer.

It is evident from a casual glance at conditions throughout the world that plant food manufacturers and agriculturists realize that "potash pays," to quote a familiar potash slogan, and a steady annual increase in consumption is expected by producers.

In the midst of all this discussion about fertilizer or plant foods, the question naturally arises as to the condition of affairs in this country as related to certain other countries of the world. France occupies a most strategic position in the international fertilizer picture, controlling the North African phosphate deposits, the potash deposits of Alsace, by-product production of 1,500,000 tons of basic phosphate slag, and more synthetic nitrogen plants than any other country in the world. Any reference to French efforts to develop domestic production of atmospheric nitrogen naturally brings to mind the government-operated nitrogen plant at Toulouse. This plant was designed to produce 150 tons of synthetic nitrogen daily, that is, approximately 52,000 tons per year. But notwithstanding the large amount that has been appropriated by the National Treasury, this plant has made a poor showing to date. Production at the government-operated plant in Toulouse during the first quarter of 1930 averaged slightly over 55 tons of nitrogen daily, that is, at the rate of 19,000 tons a year, and even though France may have more synthetic nitrogen plants than any other country in the world, domestic nitrogen output is still insufficient and im-

ports during 1929 included 400,000 tons of Chilean nitrate and 150,000 tons of ammonium sulfate.

Following the conclusion of the war and the cession of Alsace by Germany, France became an important producer of potash. In this connection it is interesting to note that domestic consumption of this item in agriculture, which was only 60,000 tons (K_2O) in 1913, has risen to the present rate of 240,000 tons annual consumption. If the rate of increase is maintained, France will soon surpass the United States in the use of fertilizer potash.

Unlike France, Germany is deficient in phosphates and over-supplied with nitrogen, and last year used in agriculture alone almost as much nitrogen as the United States used in agriculture and industry combined. Since 1913, agricultural consumption of nitrogen in Germany shows an increase of 143 per cent, potash 67 per cent, while phosphoric acid has remained stationary. Whereas in the United States phosphoric acid forms the base of the fertilizer industry, Germany uses almost 1.4 pounds of potash (K_2O) to each pound of phosphoric acid (P_2O_5) and ammonia (NH_3).

This mention of the relative proportion of use of the three basic fertilizer materials brings out the interesting point, which is generally known, that a preponderance of that material is used which occurs in the greatest abundance in the country under review.

Previous reference has been made in various instances to the fertilizer situation in the United States. Our position by comparison with the rest of the world, and judged as well by a purely arbitrary standard, should be the cause of considerable satisfaction. We have ample supplies of phosphate rock and it is to be expected that this particular branch of the industry, especially through the application of scientific research, will show greater returns. Our position in regard to potash, while unsatisfactory for many reasons in years past, is today satisfactory not only because we are now producing 20 per cent of our domestic requirements with prospect of increasing our home output, but our relationship with French and German sources of supply are upon a most friendly and coöperative basis.

The domestic nitrogen situation is considered with mixed emotions, depending upon whether the viewpoint is that of the producer or of the consumer of this commodity. Without expressing any opinion on Muscle Shoals, it is a fact that the uncertain aspects of some phases of the situation have had an effect upon the establishment of a domestic nitrogen industry. Uncertain factors of any kind, especially if they assume some magnitude, and the Muscle Shoals problem is in this class, have an unsettling effect upon industrial developments. But leaving aside any observations, the present facts indicate that atmospheric nitrogen is now being fixed at a half dozen or more plants in this country scattered at strategic points from coast to coast, and these are on the whole more modern and

efficient than most of the 100 atmospheric nitrogen plants scattered throughout the entire world.

Our position with regard to finished fertilizers, that is, the compounded plant food containing varying quantities of nitrogen, phosphoric acid, and potash, which is what the farmer buys and consumes, is no different from that of many other industries. Our domestic plant capacity approximates 12,000,000 tons a year and our annual production may be roughly stated at 8,000,000 tons a year. There is ample production facility together with adequate "know how," but the crux of the problem falls in the field of distribution. The farmer should have more plant food and the manufacturer wants to get it to him. To accomplish this there are many new ideas now in the course of formulation. Some of these ideas are adaptations or improvements of existing practices but others, and these are probably of the greatest significance, are of entirely new character. The fertilizer industry as it exists today is inherently international and as time goes on, especially through the application of scientific research, new influences will be felt in the industry which will probably have a marked effect upon it. These influences may be foreign either from the standpoint of nationality or because they arise from American interests which are not today identified as a part of the fertilizer industry.

It is impossible as well as unwise to attempt to prognosticate, but few industries offer as interesting a future as does the plant food industry. The industry is bound to increase in size as well as in importance. Soil conditions will eventually necessitate fertilization of the acreage devoted to the cereal crops and to our pastures. On the other hand, however, actuarial statistics lead us to believe that we shall reach a maximum population of approximately 150,000,000 in the next twenty-five years; this estimate varying according to authority consulted, and that the population of the country will remain fairly constant thereafter at a given figure. If these deductions are correct, we can calculate the approximate amount of our future food requirements, but who can attempt to forecast what synthetic substitutes may be introduced to take the place of our daily bread and butter, or on the other hand, who can estimate the future industrial demands upon agriculture for raw materials? In this respect cotton, the agricultural crop which consumes the greatest amount of fertilizer, is a raw material for industry. The rôle that the chemist is now playing in the fertilizer field is rapidly being extended to the field of chemical utilization of products from the farm. All this points in one direction, and in addition to such slogans as "Better Crops with Plant Food" or "Fewer Acres with Greater Profits," there might be added "Double the Industry by 1940."

It is seldom a man's mind is weakened by the burden of thought.

WHAT ARE THE STARS?*

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From the earliest days when man, in a conscious moment, began to glance skyward and observe these simple points of light, he has persisted in asking this question, "What are the stars?" It can be of little consequence to us now that medieval men regarded them as the lamp houses of heaven, which were lighted by the angels, or that they thought they had a very close influence upon human affairs. Yet, out of the early astrology has grown modern astronomy and astro-physics, just as out of the early and crude magic of the alchemist has come about modern chemistry.

Of course, the most important current news in astronomy has been the discovery of the trans-Neptunian planet. This leads me to mention that the chief difference between the planets and the stars to the ancients was merely the matter of their motion. They had no way whatever of distinguishing the physical characteristics of the heavenly bodies. The very name "planet" was given to certain of these bodies from the fact that some of them wandered about in the sky, while the majority of the stars they saw remained fixed.

It was a long time from the early attempts at a geocentric picture of the planets to the heliocentric system as we understand it today, in which we have the sun at the center, with Mercury, Venus, the Earth, Mars, Jupiter, Saturn, Uranus, Neptune, and now the new trans-Neptunian body, if it shall be verified, all circulating about the sun.

This picture of the planetary system has served as an important analogy for our comprehending some sort of a representation of the way in which electrons go around about the atomic nucleus, one which has served many a useful purpose. But little by little that picture has had to go. We can no longer indulge in a visualization of energy as so continuous a performance. The mechanism of the Bohr atom, with its jumping electrons, was an important modification of our atomic model. Yet Dr. Dushman (*1*) has pointed out the absurdity of a theory of radiation which visualizes the little electron going out and in to wherever it wants to go, and then disappearing before it gets there, but arriving at its destination none the less.

So we see that the simple picture of the solar planetary system no longer suffices to explain the nature of atomic radiation, yet in explaining many phenomena it is often convenient to have recourse to both these older and newer theories. To a certain extent physics and chemistry sometimes demand theories characteristic of a Dr. Jekyll and Mr. Hyde. In our present somewhat dualistic state of mind, we may never know when we are to meet one and when we are going to meet the other.

Passing from a conception of creation when planets were mysterious

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"wanderers" among the fixed stars to the present-day conception of galactic systems of several billion suns swirling in spiral streams, at velocities of several hundred miles per second, one may well pause to recapitulate what has happened in science to so alter man's picture of the cosmos.

A physical picture of the stars as sources of enormous radiation, and the resulting problems of stellar constitution, did not come about until the middle of the nineteenth century. Perhaps one may best regard the year 1859 as that of the birth of astro-physics. That year saw the introduction of the spectroscope to astronomy, with the concomitant interpretation, by Kirchoff, of the Fraunhofer lines in the solar spectrum. It was then that astronomers, physicists, and chemists first joined hands in divining the contents of these cosmic crucibles—the stars. Through the analysis of light rays, man has come to learn a unity and universality in the elements beyond the expectations of any medieval alchemist.

In the accompanying illustration (Figure 1) we have a rough classification of the stars by their spectral types.

First of all, taking the stars in the order of their temperature, the hotter and bluer stars are represented by spectral bands very similar to what you see on the top of this diagram, where the characteristic lines we recognize there compose the well-known series of hydrogen.

The second group of stars corresponds very closely to what we call the *F* and *G* types in the Harvard classification.

In the third group, still less of the blue end of the spectrum shows. Here many metallic lines and bands appear. The bright red stars, such as Betelgeuse and Antares, belong to this class.

And then there are a very few faint stars of the deep red type. Both of these last two types, exhibited in the third and fourth bands of the illustration, are distinguished by banded spectra, indicative of the oxides of many of the elements.

With the possibility of spectral analysis came the possibility that we could study the stars as we study chemicals in the laboratories. The attempt to arrange stars in the order of their spectral types led at once to some sort of scheme of stellar evolution, and it was believed, until the last two decades, that we were to think of stars starting at high extraordinary temperatures, 20,000 degrees or something of that sort, and gradually cooling down as they emitted their heat and energy until they fell into the invisible class, down below the dullest red stars we can observe.

This sort of scheme of evolution held until we began to discover on a statistical basis that there are two distinctly different groups of stars of practically the same spectral type. But of this we will say more later.

For a long time, many nebulous objects were thought to be possible groups or clusters of stars. Many of the so-called nebulae of Herschel's day became resolvable in his giant telescope.

FIGURE 1.—SECCHI'S TYPES OF THE FIXED STARS

If a telescope of large enough dimensions were constructed, it was thought at one time that perhaps all nebulae might be split up into a number of different stars. That question was settled when Sir William Huggins first applied the spectroscope to the telescope. Finding no continuous spectrum but just a series of bright lines, Huggins knew he was not looking upon stars, but that he was looking upon a glowing gas.

The Orion nebula (Figure 2) has a very strong green line, which until recently was supposed to be due to a hypothetical substance called nebulium. This reminds us that a strong yellow line discovered in the sun's chromosphere at the eclipse of 1868 led to the then called hypothetical substance, helium. The green nebulium line, however, does not appear to lead us to discover any really new element, for within the last few years it has been shown that there is no such mysterious substance as nebulium. Bowen, working at the California Institute of Technology, has been able to produce the characteristic green line in the laboratory from luminous nitrogen and oxygen in a very high state of electrification. So you can see that this nebulium gas has vanished literally into thin air—highly ionized oxygen and nitrogen.

Such photographs undoubtedly suggested to the cosmogonists that stars had their beginnings in a nebulous state, and that the whole question of studying the evolution of matter from the arrangement of the stars in sequence seemed to be largely a question of temperature.

With the ability of the spectroscope to discover in nebulae more primitive forms of matter than were found in the stars themselves, it became the ambition of astronomers to try to arrange in an evolutionary sequence all cosmic objects in such a way that their spectra might proceed by definite steps from the bright-line type of the gaseous nebulae to the banded spectra of the dullest red stars. With the problem outlined, rapid progress was made by Father Secchi in Europe, and Pickering and his co-workers at the Harvard Observatory in this country.

If we examine the first group of stars, then, according to the Harvard classification, we will have two or three subdivisions, *B*, *A*, and *F*. In the second main group we will have a large number of stars in about the state of our sun. For convenience we recognize subdivisions which we will call *F5*, *G*, and *K*. In the third group we will have chiefly the *M*'s, composed of red stars, many of which vary in brightness. The fourth group is called, on the Harvard scheme, the *N* type. Now we have some spectra which seem to be intermediate between those of the stars and those of the nebulae. Stars giving such spectra show bright lines in addition to the usual dark lines. These are the *O* stars. If we start with nebulae and the *O* stars, we have a group of objects first giving brilliant characteristic emission lines; we can follow through with a sequence all the way from the emission spectra of the nebulae down through the *M* and *N* groups of stars.

FIGURE 2.—GREAT NEBULA IN ORION

Now an interesting discovery should be mentioned in connection with studies of the early type. In 1892, Professor E. C. Pickering, formerly director of the Harvard Observatory, discovered in a peculiar star photographed in the southern sky, a series of lines in the spectrum which appeared very much like a hydrogen spectrum, yet the position of the lines did not fit the hydrogen spectrum at all. For some time this series of lines was called the Pickering series in hydrogen. We know now that this series of his is due not to hydrogen but to ionized helium, that is, the mutilated helium atom with one of the electrons knocked off. This was discovered by the English physicist, Professor Fowler, who long tried to obtain the Pickering series in the laboratory. Professor Fowler found he could obtain it from hydrogen only when the hydrogen was mixed with helium. Later he obtained the series from helium without the hydrogen at all. The trick was to send a powerful electrical discharge through the helium, thus ionizing the atoms. The spectrum of ionized helium is strongly characteristic of the *O* type and the so-called *B* type stars.

By the beginning of the twentieth century the accepted doctrine of stellar evolution was that in some strange way stars would evolve from hot nebulous masses at exceedingly high temperature—perhaps 40,000 degrees Fahrenheit. Bright stars in the constellation of Orion, giving the bluest light, were therefore thought to lie near the top of this scale, and to represent some of the stars in the earliest stage of stellar development. Other stars with characteristic stellar spectra exhibited the peculiar characteristics of certain bright lines in addition to the characteristic dark absorption lines crossing their spectra. These were thought at the time to be a connecting link between the strictly bright line, gaseous nebulae, and the earliest stages of the hotter stars. Letters of the alphabet were used in order of their sequence to represent the divisional classification of the stars observed at Harvard and after a considerable rearrangement the following order came to be generally accepted as the most likely one for a program of stellar changes:

O, B, A, F, G, K, M, N.

While all this observational work was in progress, theoretical workers had not been idle in attempting to add their contributions to the evolution of sun and stars. One of the most important advances in understanding the physical development of stars came about through the researches of Helmholtz about the middle of the nineteenth century. Helmholtz, searching for a possible source for the maintenance of the sun's heat, came to the conclusion that an enormous source of energy could be supplied through the contraction of a gaseous body under its own gravitation. Lane, of Washington, announced the curious paradox that a gaseous body contracting under its own gravitation would rise in temperature until by

virtue of increasing density it ceased to be a perfect gas. At this stage it would radiate about as much heat as would be generated by its retarding contraction and for a period would remain at constant temperature. With a continuation of contraction, however, the density would become so high that the body would no longer generate heat as rapidly as it lost it, and a decline in the temperature of the body as a whole was therefore inevitable. Helmholtz applied this law of Lane in an attempt to calculate the amount of shrinking necessary for the sun in order that it should maintain the present rate of radiation. This he found not to be over 300 feet a year in the solar diameter. Reasoning into the past, he calculated that the sun could not have been maintaining its present rate of radiation for more than about twenty million years. The discovery of radium by the Curies, and the birth of the new science of sub-atomic physics have unlocked new sources of energy that make it appear possible that the age of the sun or a star can be extended a hundred to a thousand times the duration assigned it by Helmholtz. Furthermore, the study of radioactive deposits in the earth's crust gives new evidence that the age of the earth is many times the hundred million years earlier set by the geologists.

Irrespective of the bearing of the Helmholtz contraction theory on the age of either the sun or the earth, it introduced a new element into the idea of stellar evolution. It was no longer necessary to suppose that stars must evolve from superheated gases and start their career at the high-temperature end of the scale. Indeed a cold gaseous mass, by virtue of its contraction under gravitational forces, would gradually rise in temperature, attain a critical maximum on the temperature scale, and then cool down indefinitely until it became a non-luminous body. If such were the case, stars would first become luminous as dull red bodies, highly diffused, and of enormous dimensions; gradually shrinking, the redness would change to yellow with the increasing temperature. Further contraction would result in the generation of greater heat until the star became literally white hot. The spectrum at such a stage might very well be that of some of the Orion stars corresponding to the letters, *B* or *A*, in the accepted list. Continued contraction would result in increasing density and presumably a general decrease in temperature. As the star cooled, its color would pass from white to yellow, again to red, and perchance ultimately become too faint for visibility. In these latter stages its dimensions would be many times less than that of the earlier stages in the sequence. Lockyer sprung, and in this country Russell, have been preëminent in the details of such a program of the star's development.

Red stars in the earlier stages of this evolution are giants, those in the latter stages dwarfs. The w[illegible] the giant and dwarf theory of stellar evolution. Antares, in the constellation of Scorpius, and a sin[illegible]

in the constellation of Orion, are typical giant stars. They are easily a million times the size of our own sun, which is probably quite typically a dwarf. It will be seen that this idea of a double sequence from low to high temperature and back again entails a considerable amount of unscrambling of the classification of stellar spectra previously outlined. Twentieth century astronomers are busy discovering minute differences in the appearances of the lines of spectra of the different classes which will distinguish the giants from the dwarfs among stars of the same color. Astronomy and physics have gone hand in hand for the solution of this problem. Thanks to Saha and others, who have advanced the theory of ionization, we can feel assured that the relative intensities of spectral lines will not be the same in the case of stars of low density as in the case of stars of high density. Since ionization is a function of both temperature and pressure, many more atoms will be ionized in the low density stars of any given spectral class. The relative intensities of lines of the ionized elements, therefore, afforded criteria for distinguishing giants from the dwarfs in the several spectral types.

Just what becomes of a star after it reaches the red dwarf stage is a problematical affair. A decade or so ago, astronomers would have probably said that it became a cold, dark star with no hope of rejuvenation, unless, perchance, in its ramblings through space, it collided with another star or with some dark cloud of inter-stellar matter. In such an event the energy released upon impact would be sufficient to raise the temperature of the star so that it would again become incandescent. In fact, the occasional outburst of a nova, or new star, in a previously unmarked region was usually attributed to such a catastrophe.

Our views in regard to the ultimate fate of a dwarf star have been rather seriously modified of late through the discovery of two or three extraordinary specimens of the dwarf type. The most outstanding individual of this non-conformist group is a very peculiar little fellow which hovers about the bright star Sirius. Now this companion to Sirius is altogether a faint star, giving out only about one-three hundred and sixtieth of the amount of light emitted by our sun. On the other hand, the spectrum is at of a white hot star, like Sirius itself. We know very well the distance his system, and can therefore deduce the area of a radiant surface of temperature which would just produce this amount of light, *i. e.*, hundred and sixtieth of that of the sun. The diameter of the t to be only about one-nineteenth that of the sun. Surely tar if there ever was one. The abnormality is that it is s not all the trouble. The swaying of Sirius in an orbital tional pull of its companion tells us that the s nearly the same as that of our sun. Now for neteenth the diameter of the sun and yet to con-

tain almost as much matter means that it must be made of ridiculously heavy stuff—two thousand times denser than platinum, the heaviest known terrestrial element. If an average book were made of such material, it would have to be issued in eight or ten volumes in order to be transportable. Even so, each volume would require a five-ton truck for delivery to your door. Such material is too absurd to imagine! That is just what the astronomers thought a few years ago. But be patient a moment; truth is often stranger than fiction.

In 1924, Professor Eddington, working on theoretical grounds, came to the conclusion that the excessively high temperatures in the interior of stars would so smash up the atoms that they could be jammed together into just such a mass of unimaginable density. Fortunately, there was one experimental way in which his theory could be verified. According to Einstein's newly proposed theory, light waves coming from so dense a star should be very considerably lengthened. This should be made evident in the spectroscope by a predictable shift of the lines in the spectrum toward the red. The same year in which Eddington announced his conclusions, Dr. Adams, of the Mt. Wilson Observatory, discovered this very shift in the spectrum of the companion of Sirius. Thus at last came the experimental verification of the existence of this fantastically heavy star stuff.

In the breaking down of the very atoms themselves under such conditions of temperature and pressure as must exist in a dwarf star of this type, it seems reasonable to suppose that the enormous amount of energy suddenly released may well percolate through to the exterior of the star so that what may have been previously a red star becomes a white-hot star again. Thus we may account for the white dwarf star, and at the same time provide ourselves with a new theory for a star's rejuvenation. Jeans would have us believe that our sun right now may be in a perilously unstable state all ready to "blow up" any minute through the advent of some such catastrophe. While the stars have told us much about the nature of matter by revealing it to us in unfamiliar states, a further understanding of the structure of the atom will go a long way toward helping us predict the future of the stars.

The problem of the source of a star's energy, and the necessary change of mass which must occur, points with considerable definiteness to the idea that the stars are actually radiating away into energy, the very stuff of which they are composed. The present meager data at hand, together with some possible uncertainties in our theoretical reasoning make, however, a doctrine of annihilation of matter not yet wholly secure. Perhaps there is no more delightful book on the subject than the book, "Stars and Atoms," by Dr. Eddington (*2*).

In concluding this discussion of "What are the stars?" and realizing how completely inadequately the question has thus far been answered, I can

perhaps do no better than to quote the closing words in the final chapter of Dr. Eddington's book where he says,

> I should have liked to have closed these lectures by leading up to some great climax. But perhaps it is more in accordance with the true conditions of scientific progress that they should fizzle out with a glimpse of the obscurity which marks the frontiers of present knowledge. I do not apologize for the lameness of the conclusion, for it is not a conclusion. I wish I could feel confident that it is even a beginning.

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MODERN PHYSICS—A SURVEY.* PART III**

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Schrödinger's Wave Equation

All this leads to the logical conclusion that the laws of ordinary mechanics cannot be applicable in the usual manner to problems in atomic mechanics. We have to devise some modification in the Newtonian method which will take into account the undulatory aspects of corpuscles when these are of atomic or electronic dimensions. Furthermore, it is an obvious deduction from the principle of indeterminism that all attempts to obtain from the solution of problems in atomic mechanics a definite answer regarding the occurrence of any individual event are foredoomed to failure. In view of the uncertainty in the definition of initial conditions we cannot expect a precise definition of subsequent occurrences. There must exist a measure of uncertainty in the prediction of events and hence *all that we can determine from the solution of a problem in atom mechanics is the probability of any individual event.*

The Schrödinger wave mechanics performs exactly these two functions. Firstly, it represents an undulatory conception grafted on the ordinary mechanical formulation of any problem in atom mechanics and secondly, once the solution is obtained (which is accomplished by well-known methods in the theory of differential equations), *the answer is interpreted in terms of probabilities.*

The first stage in the solution of a problem by Schrödinger's method may therefore be described as that in which we formulate the problem in the same manner as in ordinary or classical mechanics. That is, we assume an actual model of, say, the orbit of an electron in a hydrogen atom, or the motion of a linear harmonic oscillator. In classical mechanics the most general method for expressing the motion of a system is that which states the total energy (E) of the system under consideration as a function of the coördinates and the corresponding momenta. That is, the energy is expressed in terms of the kinetic and potential energies as functions of the instantaneous coördinates. Formulated in this manner the expression for E is said to be of the Hamiltonian form.

Ordinarily we would proceed to solve this problem by certain standard methods and the result would enable us to describe the motions of the different parts of the system in terms of certain orbits or paths. Thus in the well-known Newtonian problem of the planetary motions, the starting

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point is the postulate that the planet and sun exert an attractive force on each other which varies inversely as the square of the distance. This gives us the potential energy of the system as a function of the distance. Furthermore, we can express the kinetic energy of the planet in terms of its mass and instantaneous velocity. We can therefore write down an expression for the total energy. The problem now consists in the determination of the exact path followed by the earth in its motion under the attractive force. The "answer" deduced is that the orbit must be an ellipse with a major axis and frequency of revolution defined by the total energy of the system.

However, in Schrödinger's method the *use of classical conceptions ceases after we have once formulated the total energy in a Hamiltonian form.* We forget all about the model of a corpuscle moving with definite velocity in a well-defined orbit. Instead of proceeding as in classical dynamics, we now bring in the wave concept and use the Hamiltonian expression to calculate the "wave-length" of the associated undulatory motion. Thus if E represents the total energy, and V the potential energy, then $E - V$ denotes the kinetic energy at any instant and from the relation

$$(1/2)mv^2 = E - V$$

it follows that the momentum

$$mv = \sqrt{2m(E - V)}$$

and since the wave-length of the de Broglie wave is given by $\lambda = h/(mv)$ we obtain for λ in the dynamical problem the result

$$\lambda = \frac{h}{\sqrt{2m(E - V)}}$$

We now replace the motion of the particle by that of a wave-front traveling in a medium in which the velocity varies continuously from point to point. For the velocity depends upon the potential energy, V, and the latter is a function of the coördinates only. Consequently the wave-front of the associated wave-motion is continually suffering "refraction" in the field of force and the direction of the normal to the wave-front will be the same at every point as the tangent at that point to the orbit of the particle in the classical case.

Thus the problem becomes one of determining both the direction and amplitude at any point and instant of time of an undulatory motion for which the wave-length as a function of the coördinates is given by the above relation. In other words, the problem has now become one of *undulatory* mechanics, and can be formulated in terms of a differential equation which expresses the second derivative of the amplitude with respect to time in terms of the instantaneous phase velocity and of the second derivatives of the amplitude with respect to the coördinates; the partial differential

equation of the second order which is thus obtained is Schrödinger's famous equation.

Solutions of this equation are then sought which will give the amplitude as a finite and continuous function of the coördinates at any instant of time. The amplitude as a function of both coördinates and time is designated by ψ. The form of the equation is, in general, such that it is possible to express this function as a product of a function ϕ, of the coördinates only, and a cosine or sine series involving the time. Since we are also usually more interested in the equation for the "orbit," we need consider only the form of the function, ϕ. Therefore we can, in general, summarize the whole of the above process by stating that from the Hamiltonian expression for E it is possible by making use of de Broglie's equation for the wave equation to derive a certain differential equation (the Schrödinger equation) which gives the relation between the second order partial differential coefficients of a function ϕ with respect to the coördinates and the quantities E and V.

Whatever the physical significance of ϕ (or ψ) may be (this we shall discuss in a subsequent section), it is obvious that only those solutions of the differential equation can have any meaning whatever which are finite and continuous for all possible values of the coördinates. Now it is the peculiarity of Schrödinger's form of wave equation that the solutions fulfil these requirements only for certain discrete values of E, which are known as *eigenwerte* or *characteristic values*, and it is found that for the different problems in atomic mechanics *these eigenwerte are identical with the values of the energy levels as calculated by the classical Bohr theory* (whenever this is possible) or as determined from spectral observations. The corresponding solutions for ϕ are known as *eigenfunctions* or *characteristic functions*. The whole problem of solving Schrödinger's equation is, as a matter of fact, analogous with the more familiar problems in acoustics, of determining the positions of the nodes and the amplitudes of the loops in a vibrating string or organ pipe. The functions ϕ thus resemble standing waves with *the number of nodes equal to the classical quantum number of the Bohr orbit*. These functions have appreciable values only in those regions which would be occupied according to the older theory by the electronic orbits, and for distances greater than the radii of these orbits the values of ϕ decrease very rapidly to zero. In other words, the amplitude of the wave motion has values greater than zero only in the neighborhood of the classical orbit.

On the whole, the calculation with Schrödinger's eigenfunctions is more convenient than that involving matrices. While it was at first thought that the Schrödinger method and that of the matrix calculus are radically different, it was shown by Eckart, Dirac, and Jordan that both methods are essentially identical from a mathematical point of view and are, in fact, both reducible to a much more general kind of mathematics, the calculus of operators.

Significance of Schrödinger's Eigenfunction

So far we have spoken of an amplitude of a wave-motion, designated by ϕ (or ψ) and have said nothing about a "medium." It will be remembered that when the electromagnetic wave theory was first postulated it appeared necessary also to postulate a medium, the ether, in which electromagnetic waves are transmitted. As is well known, all attempts to demonstrate the existence of such a medium, as, for instance, the famous Michelson-Morley experiment, have yielded negative results, and the reason for this was provided by the theory of relativity. Furthermore, regarding the very nature of electro-magnetic energy, we have found it necessary to postulate a dualistic conception. On the one hand, in interference and diffraction we think of a wave-motion and measure wave-length (λ) and frequency (ν). On the other hand, in phenomena involving interaction between energy and atoms or electrons (as in the photo-electric and Compton effects) energy behaves as a corpuscular entity involving those attributes which are characteristic of corpuscle, that is, energy of magnitude, $h\nu$, and momentum of magnitude, $h\nu/c = h/\lambda$.

This association of wave and particle concepts is also seen to hold for electrons in Davisson and Germer's experiments, for when the mechanical momentum is varied, the wave-number (reciprocal of λ) or wave-length effective for diffraction of the electron beam varies in just the manner given by the equation $p = h/\lambda$.

Now in the case of radiation, Einstein had already suggested that the electromagnetic field in a given region determines the *relative probability* that the quanta go to different places: "In a set of interference fringes, the wave amplitude is strong at some places, and weak at others. The quanta go to the different places with a *relative probability* that is given by the wave measure of intensity, *viz.*, the *square of the wave amplitude*."[9]

Following this suggestion, M. Born has put forward a similar interpretation of ϕ^2 (or ψ^2). The square of Schrödinger's function for the "amplitude" of a wave-motion denotes the relative probability of occurrence of a certain event at a given point in space and at a given instant of time. Thus in the case of the hydrogen atom, we obtain a solution which gives the eigenfunctions for the different states of the atom, corresponding to the different possible orbits of the electron in the Bohr theory. These functions express the amplitude, ϕ, as a function of the distance (r) from the nucleus and two angles which denote the longitude and colatitude, respectively.

Schrödinger originally interpreted ϕ^2 as proportional to the relative charge density of negative electricity at a given point. Since, as mentioned already, ϕ has finite values from $r = 0$ to a value of r which is slightly greater

[9] E. U. CONDON, *Science*, **68**, 193 (1928). The writer is responsible for the italicized portions.

than the radius of the corresponding Bohr orbit, this interpretation leads to a representation of the electron in the hydrogen atom as "smeared out" in a spherical space having approximately the same dimensions as the atom.

On the basis, however, of Born's conception, the value of ϕ^2 corresponding to any given point in space merely denotes the probability of finding the electron at that point. *Thus the conception of a definite orbit is replaced by that of a certain region in the space surrounding the nucleus for which the probability of occurrence of the electron is greater than that for any other region.*

This interpretation of ϕ has the advantage that it eliminates completely all speculation regarding the physical reality of a wave motion associated with a corpuscle in motion. For ϕ may be a function of more than three coördinates, as, for instance, in the case of the helium atom where we are dealing with the motions of two electrons and, therefore, require six coördinates. Under these conditions ϕ^2 denotes the probability of the simultaneous occurrence of the two electrons in two specified positions, and since the probability of such an event is equal to the product of the individual probabilities there follows another important advantage of Schrödinger's method, *viz.*, it permits us, theoretically, at least (*i. e.*, apart from difficulties in the mathematical technic), to solve the problem of an atom containing two, or even more, electrons.

In this manner the difficulty of the three-body problem in classical dynamics does not occur in the new mechanics. For in the latter we consider ϕ as determined by the total field of force which is due to the interaction of all the electrons and the nucleus, whereas in the ordinary mechanics we must take into account phase relations among the electrons.

As has been mentioned already, this interpretation of ϕ^2 as a probability follows logically from Heisenberg's principle of indeterminism, and, indeed, supplements it by making the whole idea more precise mathematically. We thus perceive that it is the interplay of wave and corpuscular concepts which leads to the view of the new quantum theory as essentially a statistical theory. The problem of what occurs in any individual instance is left unanswered. All that the Schrödinger equation can yield is information about the probability for the occurrence of a certain event.

In statistical mechanics this point of view has been applied since the time of Boltzmann in order to solve many problems such as those in the kinetic theory of gases, in the scattering of alpha particles by thin foils, and similar phenomena. In this mode of treatment microcoördinates were introduced and then eliminated by taking statistical averages of the results. In wave mechanics, however, we avoid this procedure, since we derive the statistical probabilities directly from the solution of the Schrödinger equation. As Born[10] describes the logic involved,

[10] *Naturwissenschaften*, **15**, 238 (1927).

We regard the particles as acted upon by Coulomb forces, but the forces are not as in classical physics proportional to the acceleration. In fact they have no direct relation with the motion of the particles. Rather, the wave-field comes in between. The forces determine the variation of a certain magnitude, ϕ, *which depends upon the positions of all the particles simultaneously* (it is therefore a function in the "configuration space") *and in this manner that* ϕ *must satisfy a differential equation of which the coefficients depend upon the forces.*

The knowledge of the function ϕ permits us to calculate the course of a physical phenomenon, as far as it is determined by quantum mechanical laws, that is, *not in the sense of causal determinism but in the sense of probability.*

In classical dynamics the problem is always stated thus: Given the initial conditions in all their details, also the forces acting on the particles and the total energy, what is the condition at any given subsequent instant of time? On the other hand, we find that in the case of problems in atomic physics it is impossible to formulate the problem in this manner. Because of the indeterminacy of the initial conditions all we can state is the probability of a given condition at any subsequent instant of time. There exists a certain probability that the system shall be in a given state and also another assignable probability that it shall be in another given state.

It is in this sense that we must abandon the causality principle as applied to atomic physics. This principle can no longer be regarded as valid for individual occurrences, but rather for the *probability function*, ϕ^2. All we can predict is the manner in which this probability must vary with time. It is, therefore, in this sense only that we can still regard the causality principle as applicable to quantum phenomena.

The interpretation of ϕ^2 as a probability and the significance of this from the point of view of the classical principle of causality are still more strikingly emphasized by the method used in the new mechanics for calculating the intensity of spectral lines. On the basis of the Correspondence Principle, Bohr derived the conclusion that transitions between certain types of energy levels cannot occur, and that, therefore, the intensities of the line corresponding to these transitions must be zero. But according to both the matrix theory and Schrödinger's wave mechanics the intensity of a spectral line is given by the *probability of the coexistence* of the functions ϕ_i and ϕ_f for the initial and final states of the atomic system. That is, the intensity of any line depends upon the magnitude of the product of two functions, one for the initial and the other for the final state. In this deduction it is readily evident how far we have diverged from any classical notions of causality. For the most treasured feature of this principle is that the end state cannot have any effect on the phenomena which lead up to it. How, then, are we to interpret the wave-mechanics calculation of intensities of spectral lines? Perhaps the best way is to accept the result because it leads to the correct answer, and forget the causality principle, at least in atomic problems.

This means that our criterion for applying the principle of causality fails in the case of atomic systems. Can we ever be sure that two atoms are in the same initial state? The answer is necessarily in the negative, for in attempting to observe the state of the atom we must bombard it with atoms, photons, or electrons, and in each case the act of observing changes the state in an indeterminate manner. Hence, according to Bohr and Heisenberg, we must conclude that in the atom space and time are in some manner complementary, and we therefore can no longer apply to such cases the conceptions which we have found so useful for ordinary or large-scale phenomena.

Some Applications of Quantum Mechanics

It would take us much beyond the scope of the present paper to discuss the applications of the new mechanics to various problems of atomic and molecular structure, to line and band spectra, and still more recently to problems of chemical valency. By means of the new quantum theory, it has been found possible not only to derive all the results obtained by the older Bohr theory, but also to account for observations which could not be made to fit in with the latter. Furthermore, the theory represents, in many ways, a more logical approach toward the ultimate goal of any branch of science—a quantitative correlation of observable magnitudes.

It is, however, of special interest to mention briefly one consequence of the wave mechanics conception which is of greatest importance and yet represents a totally unexpected departure from the usual point of view.

In ordinary mechanics, we accept as a necessary consequence the statement that it is impossible for a particle ever to occur at a point in space for which the potential energy (V) would exceed the total energy (E). For instance, in the case of a vibrating pendulum, the maximum amplitude of oscillation is determined by the condition that at this point the potential energy is just equal to the total energy. But in quantum mechanics, the path of the particle is no longer confined to just that region in which V is less than or equal to E. The function ϕ, which defines the amplitude, and ϕ^2, which determines the probability of occurrence of the particle at any point are found to have *finite* values for regions which extend beyond those in which the motion of the particle would be confined according to classical mechanics. In other words, there exists a certain measurable probability (which is usually very small) that the particle will be found in those regions which, according to ordinary mechanics, are forbidden. The reason for this surprising result is evidently to be found in the Uncertainty Principle, for in atomic mechanics there is no longer any precise correlation between simultaneous value of position and momentum such as is demanded by Newton's laws.

Now let us consider the case of two regions of low potential energy (designated as regions I and II) separated by a central one of relatively high

potential energy (region III). According to ordinary mechanics, if the particle is moving in *either* region I or II, then it must *certainly remain there for all time*, unless it is supplied with additional energy from an external source sufficient to bring it over the "hill" which comprises region III. But on the basis of the fact that ϕ^2 varies continuously from one region of low potential energy through region III, into the other region of low potential energy, it follows that we can no longer regard a transition from region I to II, or vice versa, as impossible. Rather, for the certainty of classical mechanics regarding the impossibility of such an occurrence we must substitute, according to the new point of view, the existence of a finite *probability that in the course of time such a transition may occur*.[11]

It is by applying this consequence of the new theory that it has been found possible, for the first time, to obtain an interpretation of such a periodic phenomena as the disintegration of radioactive elements, electron emission from cold metals under the action of strong fields, and the photoelectric effect.

Concluding Remarks

To a large number it has seemed that the new point of view necessarily leads to an abandonment of Bohr's model of the atom as constituted of a nucleus with one or more electrons revolving about this nucleus in elliptic orbits. That, however, this opinion is not quite justified must be evident when we consider that in the very development of Schrödinger's equation in any problem the first step involves the formulation of the energy in terms of a model. It is only the mathematical method of solving the problem which has been modified, but the electronic orbits must still remain. Perhaps they emerge in not quite as concrete a form as the older theory represented them. The simple elliptic orbit is replaced by an annular shape, or some other more complicated spacial figure at all points of which we may regard the electron as located at any instant with a certain measure of probability.

The picture has, as it seems, become more "fuzzy" on the edges; this must be so because of the essential indeterminism in our knowledge of phenomena within the atom itself. But for the interpretation of many of the observations in atomic physics the older view need not necessarily be any less "true" than it ever was. For, after all, a scientific theory is a framework wherein we may fit together the broken parts of a picture puzzle, and, oftentimes, if we are content to select a small number of parts, the framework may be made to appear a little less complicated.

Yet, granted all this, the fact remains that we must recognize the same dualism in regard to both matter and radiation. Whether we shall ulti-

[11] This conception has been very thoroughly discussed by R. W. GURNEY and E. V. CONDON, *Phys. Rev.*, **33**, 127 (1929).

mately find a monism behind this dualism, only the future can reveal. If this event does occur, it will be because of additional experimental observations which cannot be adapted to conceptions held valid at present.

Philosophically, the doctrine of indeterminism and its consequent deduction that atomic phenomena are governed by laws of probability, will appear to many as an extremely unsatisfactory denouement for a branch of science which hitherto has always prided itself on the preciseness of its deductions. P. W. Bridgman, in his extremely interesting book on "The Logic of Modern Physics," has expressed this feeling in the following remarks:

> In general, we cannot admit for a minute that a statistical method, unless used to smooth out irrelevant details, can ever mark more than a temporary stage in our progress, because the assumption of events taking place according to pure chance constitutes the complete negation of our fundamental assumption of connectivity; such statistical methods always indicate the presence of physical complications which it must be our aim to disentangle eventually.

And from a pure philosopher comes the complaint that physics has now become metaphysics![12] Perhaps the philosopher may be excused for not understanding Schrödinger's equation.

What does it all mean? Are there structures beyond the electron and the quantum, as Bridgman would suggest? Must we conceive nature to be ultimately simple, just because we have an esthetic predilection for such a conception? On the contrary, the history of science teaches us that as we search deeper into the mysteries of nature, the more complex does it appear, and hence there is no reason, except that of mental inertia, for expecting nature to remain always simple—by which we mean that we can make mechanical models which will show us how the "wheels go round." It would, of course, be extremely convenient if nature could always have arranged things to suit our standardized modes of thinking at any period. But the history of human progress has been one in which vision and interpretation have grown with actual knowledge, and therefore we must not be shocked too severely if the present ideas of quantum mechanics appear on the one hand as a negation of our fondest expectations of the past, and on the other, a mass of abstract and almost transcendental mathematical notions. Time will undoubtedly breed familiarity and, perhaps ultimately, disdain for the "simple" ideas of the present. But that the future will reveal to us still more complex phenomena and that these in turn will necessitate still more radical ideas—these things none dare deny.

(*Concluded*)

[12] W. DURANT, "The Mansions of Philosophy," p. 64. It is worthwhile for any scientifically trained person to read the remarks of Dr. Durant, for it is always of interest to see ourselves as others see us, even if we believe them to be mistaken.

ALCHEMY: FOLLY OR WISDOM?

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The pursuit of health, wealth, and happiness has engaged the human race from its beginning, and alchemy was one manifestation of this endeavor. It is usually thought of as an attempt to change base metals into gold by means of an ill-defined something called the Philosopher's Stone.

Generally misunderstood, usually criticized or condemned, frequently ridiculed, this movement which occupied the attention of some of the best minds for almost twenty centuries was in reality something more than a get-rich-quick scheme, a gigantic patent medicine campaign, or a foolish attempt to bring heaven down to earth. Fakirs and charlatans often used it as a cloak under which they tried to deceive and despoil their credulous followers, but what profession has ever been free of unscrupulous or self-deluded practitioners?

It is not fair to judge or deride the faults or failures of the past by comparison with the supposedly superior attainments of the present; the accomplishments of one age are not intrinsically greater than those of another. Appreciation of the endeavors of a given period comes only from an understanding of the knowledge and philosophy extant at that time.

Examined from this viewpoint, alchemy appears not as pure fraud or a chasing of the rainbow; but stripped of all the magic, sorcery, and astrology usually associated with it, the art emerges as an honest effort to promote human welfare. Alchemy was both a philosophy and an experimental science, and transmutation was its end only in so far as it would give final proof of certain philosophical notions concerning the universe. One alchemist wrote:

> Would to God all men might become adepts in our art, for then gold, the great idol of mankind, would lose its value, and we should prize it only for its scientific teaching.

Many fantastic legends have been handed down as to the origin of alchemy. Some held that Adam lost the great secret when he lost Paradise; others believed Ham or Shem (Chem), son of Noah, secretly took the knowledge into the ark, perpetuating his name in the word "chemistry." Moses was said to have learned the art from the Egyptian priests and so later he knew how to burn and grind the golden calf to a powder which he "strewed upon the water (*i. e.*, dissolved) and made the children of Israel to drink of it"—probably the first record of the gold cure.

In reality, the word "chemistry" is probably derived from the sacred name for Egypt, *Chemia* (the black of the eye), descriptive of the blackness of the soil, the source of that country's wealth. Adding the Arabic article "al" gives "alchemy," the Egyptian or black art. The Egyptians were skilled in many industrial chemical arts, and trade secrets were handed down by word of mouth or by manuscripts written in cryptic language. The temple mysteries and pseudo miracles were often chemical demonstrations employed to awe the worshippers.

These chemical secrets, and especially recipes for making alloys that looked like gold and silver, were carried into Europe by the Arabs. Progress of the art was steady. By the fifteenth century, alchemy was cultivated throughout all of Christendom, reached its highest development in the seventeenth century, and then rapidly declined but never died.

The transmutation of the elements and rejuvenation of the old occupy eminent chemists today. As knowledge increases, the doubters and skeptics are crying, "It can't be done!" with less assurance.

The quest of the alchemist was a logical consequence of his ideas concerning the structure of the material world. He believed all substances to be made of one prime material, endowed with varying proportions of earth, air, fire, and water. Photographs of paintings representing these four Aristotelian elements are reproduced on pages 2666–9.* These elements were not what we now denote by the same terms, but were proper-

* Mr. David D. Nachemsohn, of Nachemsohn of London, Inc., Magasin d' Antiquités, 910 North Michigan Boulvard, Chicago, Illinois, has furnished us the following information concerning these paintings: "They are Flemish, 17th century, painted by Johann Breughel, 1569 to 1625, and their present location is at the above address."

AIR

AIR

EARTH

FIRE

FIRE

WATER

ties; thus fire signified the qualities of hot and dry; air, hot and moist; water, moist and cold; earth, dry and cold. Later three other "principles" were added, sulfur being held responsible for color and combustibility; mercury for metallic properties, and salt for resistance to the action of fire.

With these basic notions, the alchemist believed that all materials pass from one form to another by the mere addition or subtraction of the proper quantity of these so-called elements, just as water passes into ice or steam when heat is taken from or added to it. All nature was thought to be a series of transmutations and existence an eternal "flux."

To what extent and by what methods could man then hasten or retard these transitions? "God alone can make these principles out of the elements," says Basil Valentine, "but man can alter their proportion in a material and thus effect transmutation."

Gold was held to be the most perfect metal, since it does not tarnish, resists the action of fire, and does not dissolve in ordinary liquids. Silver was less noble, and lead the basest metal. Each metal was considered to be intimately connected with one of the planets, gold with the sun; silver with the moon; iron with Mars, *et cetera*, and its formation or growth was believed to be under the influence of one of the heavenly bodies.

Consequently, correct astrological conditions were necessary for the success of certain experiments. Metals were supposed to grow in the earth, and mines were sometimes closed for a while that the supply of metal might be renewed.

> All metallic seed is the seed of gold, for gold is the intention of nature in regard to all metals. If the base metals are not gold, it is only through some accidental hindrance. Nature seeks and demands a gradual attainment of perfection,

writes one alchemist.

Transmutation then became the stripping off of the ignoble properties from a base metal, or a short cut to perfection might be found in the Philosopher's Stone, a material so powerful and so full of virtue that its presence would consummate the change. Those who claimed to have seen it usually described it as red or yellow powder. Its potence was declared infinite by some, limited by others.

Since the Stone was held capable of ennobling metals its powers were soon extended to healing the sick or even to prolonging of life. "It is sought by many, found by few. It is beheld from afar and found near. It has the power of all creatures—it heals all dead and living bodies without other medicines. There is nothing like unto it under Heaven."

The fabled age of the Biblical Patriarchs was ascribed to the Great Elixir, and with its aid its fortunate possessor could secure wisdom, strength of moral character, and be lifted to a higher plane, that is, transmutation of the soul.

BRAUNSCHWEIG, GEMÄLDEGALERIE No. 358
TH. WYCK, DER ALCHYMIST
F. BRUCKMANN A.-G. MÜNCHEN

The Stone brings to each succor in his needs; it rids man of vain glory, of hope, of fear; it takes away ambition, violence, and excess of desire; it sweetens the hardest adversities. God will place among His saints the adepts of our art.

What were the experimental facts warranting belief in transmutation? Iron dipped into a solution of copper sulfate became coated with copper and apparently had been transmuted. Mixtures of base metals when melted produced yellow or white metallic products, seeming to approach gold or silver. Smelting of ores produced metals through loss of ignoble qualities.

Modern chemical analysis has shown the fallacy of considering such cases as transmutation, but the alchemists cannot be blamed for not using knowledge then non-existent. "All that glitters is not gold" has taken on a new significance since the days of the hermetic art.

In an age when magic and sorcery were accepted facts, alchemy, both chemical and medical, was believed possible. Impoverished rulers supported adepts who often came to violent ends through inability to deliver gold or cure ailments. "I once knew how to fix mercury, but now I myself am fixed," read the placard on the gibbet of one unfortunate.

The writings of the alchemists are a strange conglomeration of truth and fiction, expressed in an obscure jargon. The unscrupulous, having nothing to record, took refuge in studied unintelligibility, but even the honest workers, lacking clearness in their ideas or fearful of publishing so great a secret, reveled in the use of allegories, symbols, magical formulas, and meaningless vaporings.

Hide the sacred secret, which ought not to be disclosed to any one, nor given to any prophet.

Many of the recipes are descriptions of straightforward chemical processes but difficult to translate because even common chemicals were referred to as varicolored beasts of the fields and birds of the air.

Disregarding the quackery, the contributions of the alchemists were the discovery and preparation of numerous new and important chemical compounds and procedures, and the investigation of the medicinal properties of many materials.

They combined speculation with laboratory practice, laying the foundation of modern chemistry, and handed down an insight into nature, to be used by their successors who had fuller knowledge and better equipment. Liebig asserted, "Alchemy from first to last was chemistry."

The better class of alchemists recognized their failures, and in despair one wrote:

Now I see I know nothing, only I must not say so. For I should lose the good opinion of my neighbors, and they would no longer entrust me with their money for my experiments. I must, therefore, go on saying that I know everything.

FRANKFURT, STÄDELSCHES K.-INST. No. 216.
JAN STEEN, ALCHYMIST
F. BRUCKMANN A. G., MÜNCHEN

Another, discussing his fellow-workers, wrote:

> These do not give themselves up to ease and idleness, but they devote themselves diligently to their labors, sweating whole nights over fiery furnaces. They do not fill their time with empty talk but find their delight in their laboratory.

The modern chemist does not believe transmutation to be an idle dream. Nature accomplishes the change of elements into each other by radioactive processes, but these changes cannot be controlled or initiated in the laboratory.

It is recognized that any transmutation will cost many times the value of the product. Perhaps a catalyst, a modern substitute for the Philosopher's Stone, may be found, and if once the stores of atomic energy are unlocked, even that "life force" which distinguishes living from inanimate matter may be hoped for. The Great Elixir of Life will then be a possibility.

APPARATUS FOR SUPPLYING AIR UNDER PRESSURE

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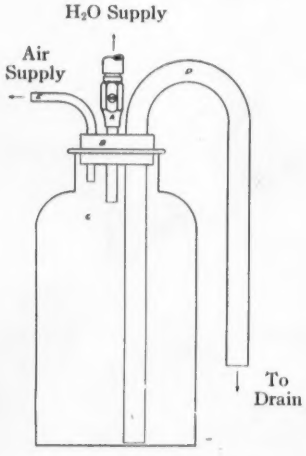
For laboratories unequipped with air pressure supply or wherever an economical and efficient air supply is necessary to operate blast-lamps, blow-torches, bubblers or stirrers, the simple apparatus here described is worthy of consideration.



AIR-PRESSURE GENERATOR

An aspirator *A* (any medium- or large-sized filter pump) projects through a rubber cork *B* into the receiver *C*, a wide-mouthed bottle of 4 to 6 liters capacity. A siphon *D* of 15-mm. glass tubing carries off the delivery from the aspirator; a 6-mm. piece of glass tubing *E* inserted in the stopper delivers the air under pressure.

Within reasonable limits the operation of the apparatus is entirely automatic, the siphon and pressure removing the incoming water, thus supplying a continuous and uniform air supply.

Nitrogen Fixation Prize. The French Chemical Society has received from M. le Bel the sum of 10,000 fr. for the foundation of a prize for the study of the transformation of atmospheric nitrogen into ammonia by algae or micro-organisms living in water.—*Chem. & Ind.*

SOME CONSIDERATIONS OF A SIMPLE PHASE-RULE STUDY*

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Periodically there appear in the literature descriptions of the preparation and the properties of substances characterized as compounds whose right to that title is seriously in question. It is perfectly possible by suitable drying processes to make some efflorescent hydrate assume any desired formula. Insufficient removal of the mother liquor causes it to appear to have a high percentage of solvate; while overzealous drying, even by such mild methods as the use of the filter paper, may make its analysis represent a solvate much lower than that originally in equilibrium with the saturated solution.

One of the problems which the physical chemist is frequently called on to solve involves the characterization of solid phases in a three-component system containing, let us say, a solvent such as water, and two solutes such as two salts with a common ion. The simplest possible case is that in which any one component appears in the solid phase. The methods outlined for the next case will readily be understood to give a solution to this problem. The second case is that in which both the original solutes appear in the solid phase. Compound formation is but one possibility, the others are that the two solutes are merely crystallizing together or that they are forming one or more series of solid solutions. Finally, of course, the solid may be found to contain all three components in the form of a compound, or of one or more solid solutions. Of these the second case, in which two of the three components appear in the solid phase, is the more frequently met and will be the principal case dealt with in this discussion. When two of the three components appear in the solid phase what may be the actual form of that solid, and how are the various possibilities distinguished?

The possibilities may be shown by making up a system containing the three components, cooling to the selected temperature, and then analyzing the solution and the solid phase.** For this preliminary treatment it is assumed that the solid can be completely freed from mother liquor and that the complete analysis of solid and solution phases can be made. It will be shown later that it is possible to construct the phase diagram if neither of these conditions is fulfilled. After the first system is determined, add some more of one of the components and repeat the above processes, thus giving for the two systems analyses of the solid and the solution phases.

There are three possibilities: (1) the composition of the solid in the two systems is the same but that of the solution varies, then the solid is a definite

* This work is part of the program now being carried out at Cornell University under a grant to Professor Bancroft from the Heckscher Foundation for the advancement of research established by August Heckscher at Cornell University.

** By solid phase is meant the total solids, whether these consist of one or more separate substances.

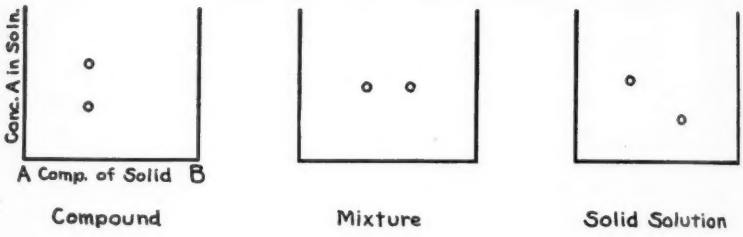


FIGURE 1

chemical compound; (2) the solid composition varies but the two solutions are identical, then the solid is a mixture of the two solutes; (3) both solid and solution phases differ in composition, then the solid is a solid solution of the solutes.

The criteria for the three possibilities may be expressed graphically in Figure 1, where are shown the diagrams of the three-component system, two components in the solid phase and at constant temperature. In these diagrams the concentration of A (or B) may be expressed either as grams A per gram of water or as grams A per gram of solution; the solid composition may be expressed as mol per cent or weight per cent.

This preliminary exploration will need extension and the complete diagrams for these systems may have such appearance as those following, in Figure 2.

These diagrams may be explained first by the phase-rule method. The derivation of the phase rule leads to the algebraic expression, $F = C + 2 - P$, in which F represents the number of degrees of freedom, C the number of components, and P the number of phases. The number 2 in the expression represents pressure and temperature which are ordinarily assumed to be the only independent variables. When additional variables are included the number two must be increased to accord with the new assumptions. In the systems containing two salts with a common ion dissolved in water $C = 3$, and the phase rule becomes $F = 3 + 2 - P$. Since we choose to work at a fixed temperature, the number of independent variables is reduced to one and the expression becomes $F = 3 + 1 - P$.

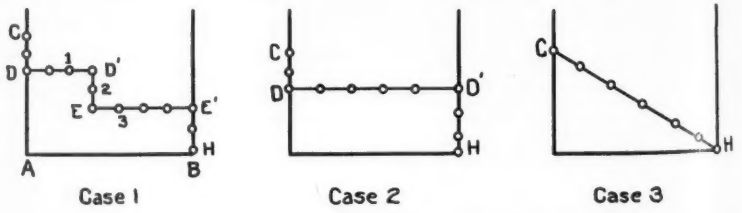


FIGURE 2

If $P = 3$ (one solid, solution, and vapor phases), then $F = 3 + 1 - 3 = 1$. Having fixed the temperature and required that there be three phases we have a univariant system, having one degree of freedom and permitting either pressure or concentration of the liquid phase to be altered independently, but not both. If, however, $P = 4$ (two solids, solution, and vapor phases), $F = 3 + 1 - 4 = 0$. There are now no degrees of freedom; the system is invariant, the composition of the liquid phase is fixed and can have only one value at the temperature chosen. This means that in the three-component system with the two salts A and B crystallizing as a mixture (*two* solids) in the solid phase, we shall have only one concentration of liquid phase which will be in equilibrium at any given temperature and this is quite independent of the relative or absolute amounts of A or B in the solids. Since, then, we shall have only one solution phase and one vapor phase in the simple case, the variance of the system will be determined by the number of solid phases. When there is one solid phase the system is univariant; when there are two solid phases the system is invariant.

As illustrations of these principles we may consider the diagrams of Figure 2. Let C represent the concentration of a solution saturated with component A, alone. On addition of B to the system, the solubility of A usually decreases but solid A remains the single solid phase until at D, in case (1), the compound begins to come out. Now we have two solid phases, A and AB, and consequently the system is invariant, which means that the composition of the solution remains constant.* Another way of looking at it is to say that the solution is saturated with A and with AB and consequently its composition is fixed. As more B is added, A in the solid phase disappears to form AB until only AB is the solid phase at D'. Further addition of B will decrease the solubility of AB and hence the concentration of A in the solution will decrease. This variation of the solution phase is possible now because there is only one solid phase, AB. Further addition of B now, however, causes B to appear in the solid phase; two solids B and AB are in equilibrium with a solution of fixed composition along $E'E$. As other systems are prepared containing increasing proportions of B the relative amounts of AB in the solid phase continuously decreases until finally the solid phase consists of B only. Or to reverse this, starting with a solution saturated with B alone (no A, point H), increasing amounts of A may be added with increasing concentration of A in the solution until the compound AB begins to appear in the solid phase along with B at point E. The solution concentrations will then be constant again along the line EE'.

Exactly the same reasoning applies to case (2) except the two solid phases

* Except in the solid solution the concentration of the components in the solid phases is constant. The composition of the total solids may be variable.

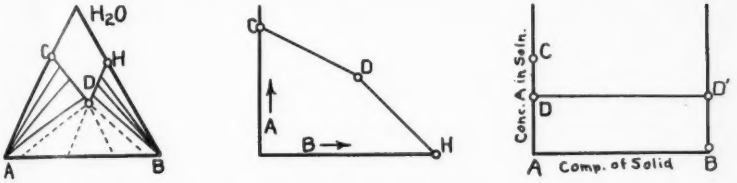
are not A and AB or B and AB but only A and B as a mixture of crystals. In both these diagrams vertical lines represent univariant systems (with only one solid phase), and horizontal lines represent invariant systems (with two solid phases). In case (3) we have a univariant system throughout, the single solid phase being a solid solution of one salt in the other. The concept of a solid solution may be reviewed. We are much more familiar with liquid solutions, say of benzene and toluene and know that the more benzene we have in solution, the more benzene will be found in the vapor phase. The solid solution of two salts will be a single solid phase of continuously varying composition (as the benzene toluene solution) and the solution in equilibrium with the solid solution will likewise continuously vary (as the vapor phase in the familiar case). The diagram of case (3) shows clearly this continuous variation in the composition of the solid phase and the solution in equilibrium with it.

This type of diagram, while very useful is not commonly met.* It seems to be a modification of Schreinemaker's diagram and the criteria discussed above were set forth by Lash Miller in 1903. These criteria cannot be accepted too blindly, for a study of only two compositions might lead to erroneous conclusions concerning the system as a whole. One might happen to strike 1 and 2, 2 and 3, or 1 and 3 in Figure 2 and conclude that the solid phase is a solid solution. Again, if the solubility of the compound is but slightly affected by excess of A or B, the line from D to E might appear straight and the compound be missed. These possible errors would be detected in a complete study of the system. This method of representation will now be compared with the diagrams that are somewhat more familiar. A comparison of graphical methods of representation of three-component systems, assuming one or two components in the solid phase, at constant temperature, is shown in Figure 3.

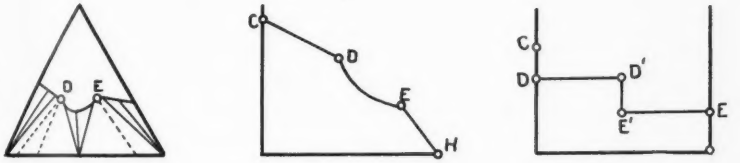
For most of us, our previous study of the phase rule has been made with the aid of the triangular diagrams of Gibbs or the modified Schreinemaker's rectangular coördinates. These three methods of representation are not mutually exclusive but mutually complementary and may be used interchangeably. Each has its advantages and its defects but probably the triangular diagram is the most generally useful. Similar systems will now be shown on each type.

In each of these diagrams C represents the solution saturated with A only, while H represents the solubility of B in water. The diagrams are all isothermals. In case I we have the simplest case of a simple mixture of two salts crystallizing out; CD represents the composition of solutions con-

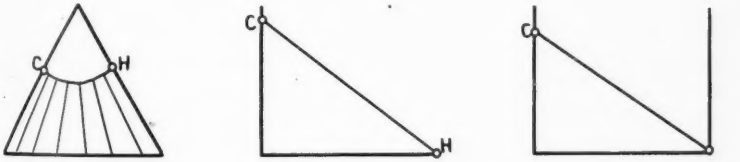
* In his recent monograph, "Equilibria in Saturated Salt Solutions," 1927, Blasdale has made use of a similar diagram plotting per cent of A in the solid phase against per cent of A in the total weight of $A + B$ in the liquid phase. This has the advantage of giving a definitely closed diagram.



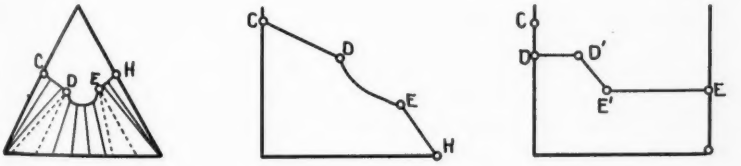
Case I. The two salts crystallize together.



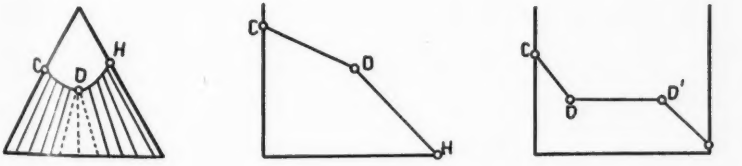
Case II. The salts form a compound.



Case III. The salts form a continuous series of solid solutions.



Case IV. The salts come out separately and in one solid solution.



Case V. The salts form two series of solid solutions.

FIGURE 3

taining increasing amounts of B and in equilibrium with solid A only. At D, solid B begins to crystallize and we have a solution of fixed composition in equilibrium with two solid phases (now an invariant system). The average composition of these solids varies from nearly pure A to nearly pure B. DH represents solutions in equilibrium with pure solid B alone. Exactly the same wording applies to the second type diagram which I choose to call the coördinate type. In general, the same considerations apply to the rectangular diagram except for one important difference. The point D of the first two types becomes a line DD' on the rectangular diagram. This point D is, of course, the most important one on the diagram. It is very important, then, that its composition may be thus emphasized. Herein lies one of the greatest virtues of this diagram.

The succeeding diagrams are largely self-explanatory. In case II at D the two solid phases are A and compound A_mB_n, at E they are compound and B, and the solutions between D and E are in equilibrium with the compound only. The rectangular diagram again shows its value in that the projection of the line $D'E'$ (the solutions in equilibrium with compound only) to the base line indicates at once the composition of the compound. The composition of the compound is likewise shown on the triangular diagram; but an inherent weakness of the coördinate diagram becomes apparent in that there is no way on it to show the composition of the solid phase. Even pure A and pure B would be at infinite distance from the origin and lines drawn from the solution compositions on CD to pure A will thus be parallel. Translating this to the triangular diagram gives a proof of the oft-repeated axiom that parallel lines meet in a point at infinity.

To summarize, then; in these three-component systems, two solid phases, a liquid and a vapor, constitute an invariant system shown by a horizontal line on the rectangular diagram and by a point on the other two diagrams. One solid, the solution, and the vapor constitute a univariant system in which the composition of the solution may be changed within limits at the selected temperature; this solution composition will be shown by a vertical line on the rectangular diagram (a curve for the solid-solution solid), and by some curve on the other two diagrams. This may well be demonstrated by a chart of the solution phase representation:

Three-Component Systems at Constant Temperature Representation

Phases	*Variance*	*Triangular*	*Coördinates*	*Rectangular*
One solid, solution vapor	1	Line	Line	Vertical line curve for solid solution
Two solids, solution vapor	0	Point	Point	Horizontal line

The Method of Investigation

But even when all this has been said, there remains some doubt as to just how much concrete significance it can have, and the question arises, how

should one set out intelligently to study such a system? As an example we might select the boric acid–tartaric acid–water system recently studied in the Cornell laboratory. Usually such a system requires the ability to analyze solid and solution for two of the three components. Actually it is possible in special cases to construct the isotherm if one can analyze for but one component. In this boric acid–tartaric acid–water system it is possible to titrate first the tartaric acid using such an indicator as bromthymol blue (6.0–7.6), which is but slightly affected by moderate concentration of boric acid. Then by the addition of excess glycerin, the boric acid may be titrated with phenolphthalein as indicator.

The first step in such an investigation should be the placing of the two solubilities of the two acids on a triangular diagram and the drawing of a line between these points. In general, this will serve to indicate that systems above the line will have no solid phase while those whose compositions fall below the line will have one or more solid phases at equilibrium. This assumes that there is no marked mutual increase or decrease of solubility exerted by the solutes. We must have solid phases so a line such as MN is drawn roughly parallel to the original line CH in Figure 4, and situated at such a distance below CH as will probably produce analyzable amounts of solid phase and of solution. Along the line MN select, say, seven points and make up the system whose compositions are thus represented. Heat to some suitable higher temperature to accelerate solution and attainment of equilibrium, cool to the selected temperature, and analyze when equilibrium is reached.

The data then at hand will consist of the compositions of the original system (overall composition) of the solid and of the solution phase when equilibrium is reached. The use of these data constitutes the next step. Most of the use of the triangular diagram depends on the fact that the saturated solution is poorer in the solid phase than the original system, or, graphically, the solid phase, the original system, and the saturated solution lie on a straight line and in that order. Of course, it requires but two of these three points to determine the straight line and it may be added that the solid phase with its adhering mother liquor may serve instead of the pure solid phase. If separation and analysis of the solid phase in the pure stable condition is convenient, this is most satisfactory for the line determined by the pure solid phase and the saturated solution will be most certain because of the relatively wider separation of these points. In numerous cases, however, isolation of the pure solid phase is difficult and, in the case of unstable hydrates, attended by the dangers of partial or complete decomposition, resulting in uncertain and erroneous results. In such cases the solid phase is analyzed together with the adhering mother liquor. The composition of this mixture also must lie in the straight line, between the original system and the pure solid phase. In such systems, a line

joining the composition of the original system or of the saturated solution with the composition of the impure solid phase will cut the side of the triangular diagram at the composition of the pure solid phase if there is not formed a ternary compound or ternary solid solution.

Now we can use the data. The analysis of the saturated solutions may give such a series of points as shown, systems, (1), (2), (3), yielding boric acid as the solid phase, (5), (6), (7), giving tartaric acid, and from system (4) no crystals appear. In this particular case it will appear that (4) gave no

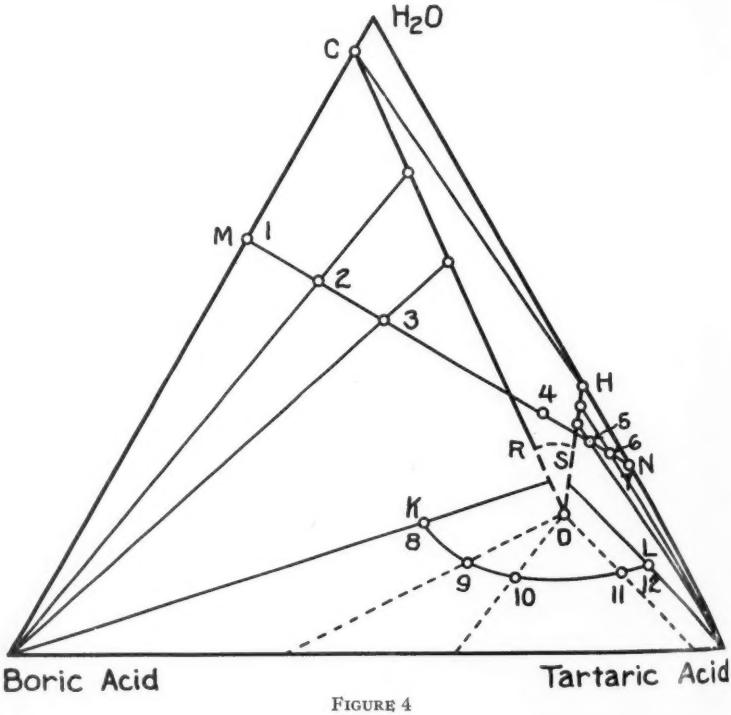


FIGURE 4

solid because of the very large mutual increase in the solubilities of the two acids. In order to determine whether *CR* and *SH* really meet in a point *D* as they appear to do and as a mere mixture of crystals requires, or whether there is formed some compound with saturated solutions on such a curve as *RS*, it will be necessary to make up and analyze a second set of systems along such a curve as *KL* so chosen as to be safely below the expected position of *D*. In the system under study, systems such as (8) give boric acid, (12) gives tartaric acid as solid phase and intermediate systems give

a common saturated solution. D is in equilibrium with various mixtures of solid boric and tartaric acids as indicated along the base line. The solid phases containing mostly tartaric acid could be analyzed readily and there the composition of the solid phase was used for determining the lines. In the boric acid side of the diagram this was more difficult and the lines there were determined by the composition of the original system and the saturated solution resulting from it. Either method is valid; the former is preferable.

The results for the boric acid–tartaric acid–water system show that the two acids crystallize together after large increases in solubility. Point D on the diagram is, at room temperature, 23–25°,

Tartaric acid	65.1%
Boric acid	12.3%
Water	22.6%

To demonstrate the large increase in solubility;

	Grams boric acid / 100 grams water	*Grams tartaric acid / 100 grams water*
Point C corresponds to	5.0	...
Point H corresponds to	..	136
Point D corresponds to	54.4	288

In other words, the solubility of boric acid can be increased ten-fold by the addition of tartaric acid; while the solubility of tartaric acid is more than doubled in the presence of boric acid. This investigation demonstrates that no solid compound of boric and tartaric acid is formed at room temperature. It does not preclude the possibility that the solution may contain such a compound as some organic chemists have postulated.

Special Considerations of the Triangular Diagram

There are certain dodges and schemes one may bear in mind in such an experiment, most of which have their origin in the properties and interpretation of the equilateral diagram with each side divided into one hundred divisions and lines drawn through these points parallel to each of the other two sides. Then each division represents one per cent and in Figure 5, the system at O contains:

$O{:}a$ % A, $O{:}b$ % B, and $O{:}c$ % C, the total being 100. It follows from this that a line joining a vertex, A, with some point on the opposite side represents systems containing variable proportions of the three components but the ratio B/C is a constant.

This enables one to make an indirect attack on the problem, removing the necessity of analyzing the solid phase. Suppose the original system were made up as D and the saturated solution in equilibrium with the solid phase is E. The saturated solution is obviously poorer than the original

system in respect to the component or components which separated in the solid phase and these are shown by extending the line joining D and E to cut the side of the diagram at the composition of the total solids separating, in this case pure A. It is emphasized that the ratio B/C is the same for D and E; E is merely poorer in component A than is D. In the making up of the systems this device can be utilized. Suppose one requires say ten grams of solution phase to analyze and is not interested in the solid except that there must be some; and suppose further that he knows about where E will lie, where shall D be selected or what should be the composition of the original system. Qualitatively, if D be close to E there will be little solid; if far separated little solution phase. This relationship holds; the proportion by weight of the solid $= ED/EA$, of the solution, $= DA/EA$. This becomes obvious if one says: "add five grams of A to five grams of the saturated solution E." The resultant system will then fall on the line AE half way between E and A. This device will, after the first main lines are known, minimize the possibility of cooling a system and finding insufficient solid or liquid phase for analysis.

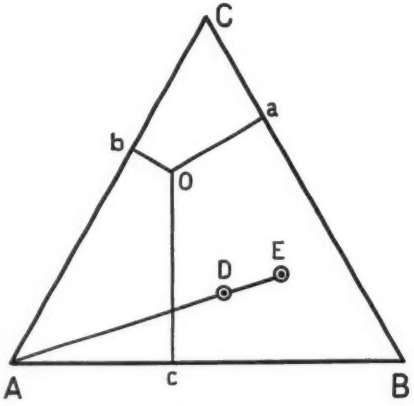


FIGURE 5

Another use of this property of the triangle can be made in the simple case if one wishes thus to investigate two acids of about equal strength. We wanted recently to find the mutual solubility effects of succinic acid and tartaric acid in aqueous solutions. Such a quantity of tartaric acid and water was taken as would make a 35% solution, R (Figure 6), of tartaric acid in water alone (considerably less than a saturated solution), and a known excess of succinic acid was added to make such a system as N.

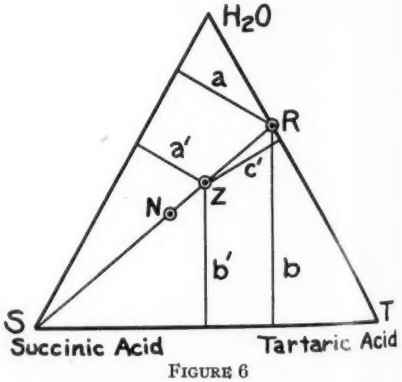


FIGURE 6

This was heated, cooled, and the solution phase titrated with alkali, titrating, of course, both acids. Suppose the composition of the saturated solution be some point such as Z. We may express per cent composition in terms of actual weight if we consider always one gram of solution. Let a = grams of tartaric acid per gram of solution R, b = grams of water per gram of solution R; and let a' = grams of tartaric acid per gram of saturated solution Z, b' = grams of water per gram of saturation solution Z, and c' = grams of succinic acid per gram of saturated solution Z.

We know that $a + b = 1$, and $a' + b' + c_1 = 1$, and $a'/b' = a/b = 35/65$, and $a'/75 + c/59$ = equivalents of acids titrated per weight of saturated solution titrated, where 75 = the equivalent weight of tartaric acid, and 59 = the equivalent weight of succinic acid.

By means of these equations one may solve for a', b', and c' and thus locate Z. This method will work, of course, only so long as only one component, in this case the succinic acid, appears in the solid phase.

The above calculations appear somewhat laborious and Professor Bancroft suggested that a mere proportion would suffice. Continuing experimentally exactly as before, one determines the amount of alkali needed to titrate one gram of the solution, Z, saturated with succinic acid. This solution is known to lie somewhere on the 35% line SR. One can easily calculate that one gram of succinic acid, S, requires X cc. of alkali, one gram of a 35% solution, R, of tartaric acid in water requires Y cc. of alkali, and experimentally one gram of the saturated solution requires Z cc. of alkali. Then $\frac{Z-Y}{X-Y}\,100$ = the per cent of succinic acid in the saturated solution.

The actual figures for this case were: (for 5.9 grams of saturated solution):

$$\frac{27.6 - 25.0}{90.7 - 25.0} \times 100 = 3.95\% \text{ succinic acid}$$

The former longer method gave 3.9% in satisfactory agreement. In this case, as in normal cases, there is a decrease in the solubility of the succinic acid. In water alone its solubility is 7.0 grams in 100 grams of water; in the tartaric acid solution its solubility is 6.25 grams in 100 grams of water.

This device may be employed also for systems containing an acid or a base together with a salt or a non-electrolyte in aqueous solution. Here the X or the Y of the above equation will be equal to zero and the rest of the treatment will be unchanged. The method probably cannot be used without alteration when the solid phase is not a pure single component.

Summary

1. The phase-rule method of treatment is outlined for simple three-component systems, with a special view of investigating the possibilities when the solid phase contains two of the three original components.

2. For distinguishing the three possibilities, two systems are prepared containing different amounts of one component, and the solid and solution phases of each system are analyzed. The three possibilities and their interpretation are:

If the solids are the same, but the solutions vary, the solid is a compound.

If the solids vary but the solutions are identical, the solid is a mixture.

If the solids and the solutions are different in the two systems, the solid coming out is a solid solution.

3. These possibilities are depicted graphically for comparison of the triangular, coördinate, and rectangular diagrams.

4. A method of attack for the study of such a system is outlined and applied to the system, boric acid–tartaric acid–water.

5. It is shown that tartaric acid increases the solubility of boric acid in water over ten-fold and boric acid doubles the solubility of tartaric acid. There is no compound formed at room temperature, the two salts crystallizing together at the invariant point.

6. The properties of the triangular diagram are utilized to permit some indirect methods of study of such a system, whereby in some simple cases the system can be constructed when one can analyze for but one component.

Hope for Burned Children Seen in Tannic Acid Treatment. Recovery of greater numbers of child victims of burns may result from wider applications of a new method of treatment, making use of tannic acid, it appears from recently reported experiments. The method was devised by Dr. Edward C. Davidson of Detroit. Recent successful results with it have been reported by Dr. W. C. Wilson, who used it in the treatment of a number of small patients at the Edinburgh Hospital for Sick Children and the Royal Infirmary at Edinburgh, Scotland.

Dr. Wilson found that the tannic acid treatment reduced the mortality from burns to about one-quarter of that observed in another comparable series of cases. As burns in children are especially apt to be fatal, these figures are particularly gratifying. The tannic acid solution is sprayed on the burned areas, which have first been thoroughly cleaned. No dressings are used and the burned area is dried, after the spraying, in hot air under a bed-cage. The spraying is repeated hourly as long as necessary.

The method controls the acute toxemia which sets in during the second stage of a burn. In the first stage there is slight shock. The second stage is characterized by a secondary shock and toxemia. This condition is due to the absorption into the blood stream of poisons set free in the severely damaged tissues.

Besides reducing the mortality, the tannic acid treatment reduces the severity of the symptoms at all stages and promotes rapid healing. It is also of especial value when considerable areas have been burned. Previously it was held that burns of 30 per cent of the body surface in adults and 11 or 12 per cent in children were almost sure to prove fatal. The results obtained in Dr. Wilson's series of cases led to the conclusion that burns of more than 60 per cent of the surface in children will cause death from shock in a few hours; that when between 35 and 60 per cent of the surface is affected the outcome depends on the degree of poisoning which has developed; but that when less than 35 per cent of the surface is burned, the chances for recovery are good, provided treatment is begun within a few hours of the injury.—*Science Service*

THE USE OF MODELS IN TEACHING POLARITY

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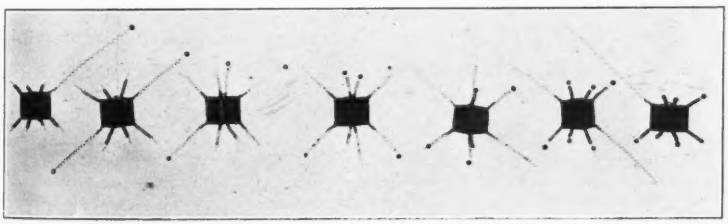
The Lewis-Langmuir hypothesis, which was first applied to the extreme cases of electron transfer and equal sharing, has been extended to apply to that great intermediate field lying between. We now have a unified concept which removes the sharp line of distinction formerly thought to exist between ionized and non-ionized compounds. We have come to realize that all compounds cannot be divided into the two classes any more than all people can be classified as good or bad. The one type shades into the other. We are handicapped, however, by the fact that we have developed no methods of precision by which we can study polarity in this intermediate field, and are forced to rely on methods of inference. Nevertheless, our understanding of the mechanism of chemical reaction is growing rapidly, thanks to the octet hypothesis.

The original theory of Arrhenius has become a historical incident in



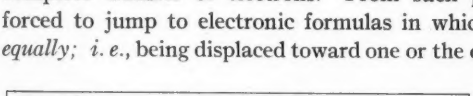
Li Be B C N O F

FIGURE 1.—SHOWING THE RELATIVE POLARITIES OF THE SEVEN ACTIVE ELEMENTS OF A SHORT PERIOD

the development of a more comprehensive viewpoint regarding the structure of matter. Viewed in the light of economy of time and economy of nervous energy, it would seem to the writer that the beginning student should be first introduced to polarity through the unified concept presented by the extension of the octet theory to cover the entire field of polarity. He gains through this concept a clearer picture of valence and ionization through electron transfer, but best of all, he includes in the same picture cases of non-polarity and partial polarity. He can then view the theory of Arrhenius in retrospect. This more complete concept can be developed quite independently of the ionization theory of Arrhenius.

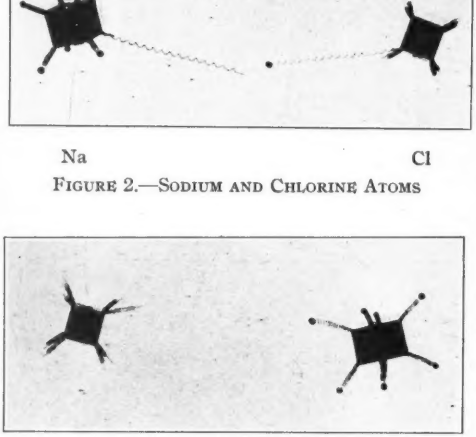
One of the great difficulties the student faces is that of transferring his mental image of the octet atom, with its electrons *fixed* at the corners, to a plane surface on which the electrons are shown in various positions about the symbol. Most of our elementary and advanced textbooks, in their projections of the atoms, show the electrons *fixed* on the corners of the cube and can thus only present the extreme cases of complete non-polarity or

complete transfer of electrons. From such projections, the student is forced to jump to electronic formulas in which electrons are shared *unequally; i. e.*, being displaced toward one or the other of the atoms. We are forcing the student to conclude that electrons are not held on *fixed* corners, but are rather held in an elastic manner which permits them to be pulled away some distance, or completely, from the kernel of the atom. Because of the difficulty the student has in making this transition in his mind, the writer has taken the liberty of building an atom model which will bridge the gap and simplify this problem for the student. The criticism may be justly made that such a concept as presented here is too concrete, and does not align itself with the existing physical evidence. Nevertheless, as long as the student is forced in his own thinking to pass through such a concept, it might as well be done for him in the most concrete manner possible, so that there will be no mistake in his understanding of the complete meaning of polarity.



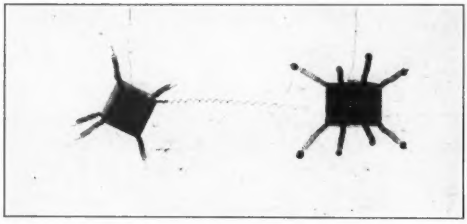
Na Cl

FIGURE 2.—SODIUM AND CHLORINE ATOMS



Na^+ Cl^-

FIGURE 3.—SODIUM AND CHLORINE IONS

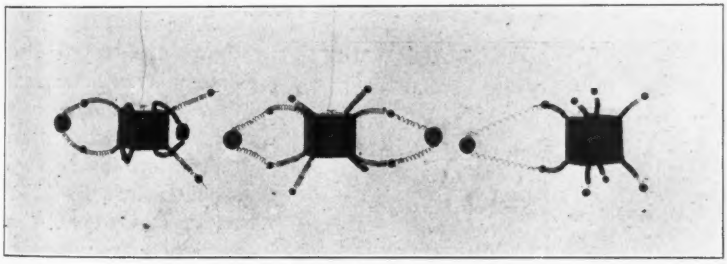


Na^+ Cl^-

FIGURE 4.—SHOWING THE ELECTROSTATIC ATTRACTION BETWEEN SODIUM AND CHLORINE IONS

In the models used by the writer to develop the idea of polarity, the kernel of the atom is a painted block of wood. It is assumed that the student is already familiar with the modern theory of the structure of atomic nuclei. Therefore, only the valence shell of electrons is shown. A copper wire spring is attached at each corner of the cube. A small finishing nail

forms a short core for the spring, and acts as a guide when coiling the spring. The coil is made slightly larger than the diameter of the finishing nail. Electrons are made of modeling clay rolled in red lead to give color. They are merely stuck on the ends of the springs where desired. The affinity of each atomic kernel for its valence electrons is shown by the degree to which the spring is coiled or uncoiled. Thus the lone, loosely held electron of a sodium or lithium atom is shown at the end of an uncoiled spring while the other seven springs remain tightly coiled. Sodium is thus concretely represented as a donor atom. The reverse case is shown in the chlorine atom, where the seven electrons are held on tightly coiled springs, with the one free spring reaching out in space for an electron. In the case of carbon, all springs are half extended, illustrating the balanced atom. Figure 1 shows the seven active elements of a short period.



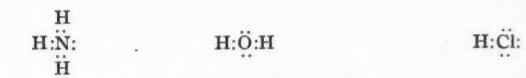


FIGURE 5.—SHOWING THE RELATIVE POLARITIES OF AMMONIA, WATER, AND HYDROGEN CHLORIDE

The transfer of an electron in the formation of sodium chloride is easily illustrated with these models. Figures 2 and 3 illustrate the transfer. After gaining its electron, the extended spring of the chlorine atom coils up, and the chlorine ion assumes a balanced position. The extended coil of the sodium ion likewise coils up. If desired, the electrostatic attraction between the sodium and chlorine ions can be indicated by leaving the one coil of the sodium ion extended toward the chlorine ion (Figure 4).

As is noted in Figure 1, the chlorine atom holds its electrons closer to the kernel than oxygen; oxygen closer than nitrogen. Thus, electron pairs of nitrogen can be brought closer to the proton of an attached hydrogen and hold the latter in a non-ionizable union in ammonia. In the hydride of oxygen, the electrons are unable to hold attached the protons in as close a union as in the hydride of nitrogen for they are bound closer to the oxygen kernel; slight ionization is therefore possible. The electrons of chlorine

are held so close to the kernel that they exert little influence on the proton of hydrogen in the hydride of chlorine. Therefore hydrochloric acid ionizes freely in a water medium, where the attached proton may come under the influence of the free electrons of a water molecule to give a hydrated ion. The relative polarities of these three compounds are shown in Figure 5.

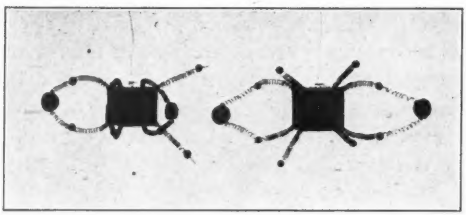
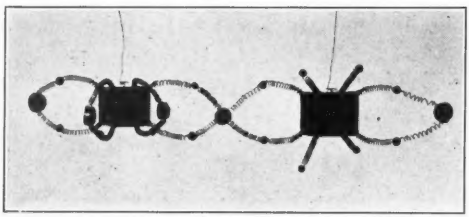


FIGURE 6.—SHOWING THE ACTION OF AMMONIA WITH WATER



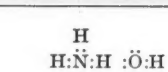


FIGURE 7.—SHOWING THE UNION OF WATER WITH AMMONIA TO FORM AMMONIUM HYDROXIDE

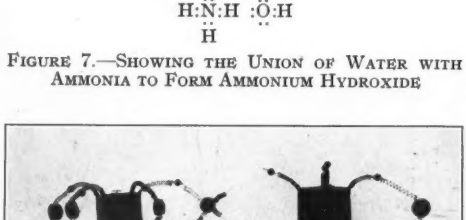


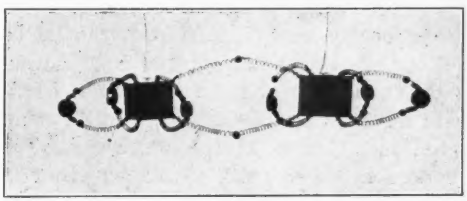
FIGURE 8.—SHOWING THE IONIZATION OF AMMONIUM HYDROXIDE

Figures 6, 7, and 8 show the reaction of ammonia with water in dissolving and forming ammonium hydroxide, and in ionizing into ammonium and hydroxide ions. Figure 6 shows a molecule of water, the proton of which is coming under the influence of the two free electrons of an ammonia molecule. Figure 7 shows the union of a water and an ammonia molecule. The attached proton is now more under the influence of the nitrogen electron pair than the oxygen pair. Also, hydrogen is temporarily given the unorthodox valence of two, and nitrogen an equally unorthodox valence of four. Figure 8 shows the separation of the molecule into ammonium and hydroxyl ions. The formation of ammonium chloride may be similarly shown.

The action of a water molecule on a hydrogen chloride molecule is similar to the action of ammonia on water. The attached proton of hydrogen chloride readily comes under the influence of a free electron pair on the water molecule forming a hydrated hydrogen ion.

Carbon may be considered a balanced atom since its tendency to give is balanced by its tendency to take. As a result it does neither completely. It merely shares electrons. The union between two carbon atoms is non-polar when both of the carbon atoms are attached to identical groups. Ethane (Figure 9) shows such a non-polar union.

Many other illustrations are, of course, possible in showing reactions of inorganic and organic nature. These suffice, however, to point out the use of such models as teaching aids. The student easily makes the transition from such models to electronic formulas on a plane surface. The older cubical form is used to represent the atomic kernel largely because most elementary textbooks still use cubical projections in presenting the Lewis-Langmuir hypothesis. However, the pairing of electrons as well as the tetrahedral form for the atom can be readily shown by bringing the ends of adjacent springs close together. Carbon can thus be shown as a typical tetrahedral atom in which each electron is held by two springs. By using this form for the carbon atom the stability of a molecule of carbon monoxide can be better understood. However, the use of the cubical form makes it difficult to show triple bonds. Undoubtedly, wooden balls would be superior to cubes for many reasons in representing the kernel of the atom. The springs could be attached to the balls in tetrahedrally distributed pairs. When the student has developed some ability to handle the concept mentally, this spherical model which lends itself more readily to the interpretation of modern theories could well be used.



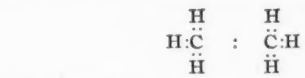


FIGURE 9.—ETHANE, SHOWING A NON-POLAR LINKAGE

The use of such models makes it possible to teach polarity to beginning students, and thus start them out with a rational view of ionic and non-ionic reactions, donor and acceptor atoms, acids and bases, solution and chemical action, hydration, crystal structure, and electrostatic forces. The models merely aid in making the concept, which is finally arrived at by the advanced student, clear to the beginning student, so that he may omit many of the laborious steps now involved in arriving at a unified view of the nature of chemical reaction through polarity.

A NEW RELATIONSHIP CHART OF THE CARBOHYDRATES*†

C. W. EDDY, 148 S. MISSION ROAD, LOS ANGELES, CALIFORNIA

It is well understood that the most effective means of obtaining knowledge is through the sense of sight. The adoption of charts and models in science courses to explain the ideas marked an advance over the pure lecture system of teaching. The student visualizes through the use of charts and models the idea that is endeavored to be expressed and fixes it more distinctly in his memory, thereby retaining the idea for a longer period of time.

History of the Relationship Charts

A relationship chart between the hexoses and the pentoses was first constructed by the author when answering a question in a course in advanced organic chemistry. The author then saw the possibility of a more complete and legible chart and after much study and reference work, the "Relationships among the Carbohydrates" (Plate I) was formulated.

Rosanoff (*1*) has an ingenious chart showing the relationship that exists between the simpler sugars and their reaction products. The difficulty with the chart for beginners lies in his method of explanation. He has given each class of compounds a symbol and additional symbols, such as dots and side arms, placed on the primary symbol indicate compounds formed from the primary compound. This method necessitates the memorizing of a group of symbols in order to understand and remember the existing structure and reactions of the sugars. In the preparation of this chart as presented, the author has endeavored as much as possible to do away with symbols except as the symbols represent the actual structure of the compounds.

Relationship and Nomenclature

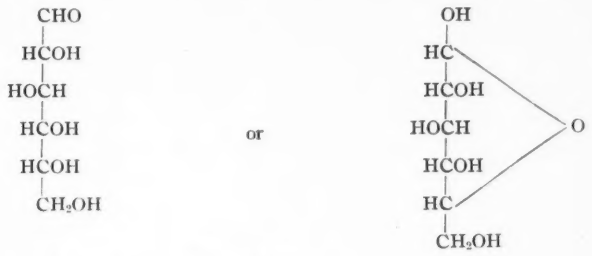
The relationships among the different forms of sugars are based on the pioneer researches of such honored men as Emil Fischer, Werner, Wohl, Kiliana, Nef, Ruff, Lob, and many others. Their patient researches have, by many experiments, shown us the structure of the sugars as they are believed to exist (*2*). They have also given us the reactions by which one form of a sugar may be converted into its isomer.

Cohen, Armstrong, Rosanoff, Fischer, Wohl, and others seem to disagree as to the naming of the forms of the sugars, especially between the *d*- and *l*-forms. Therefore it has seemed reasonable to follow the more modern

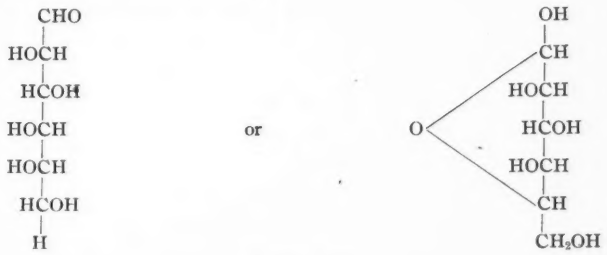
* The author wishes to express his sincere thanks to his professor, Dr. H. J. Barrett, for his suggestions in the preparation of the charts and the article.

† The presentation of a paper covering the essential features, uses and adaptations of the chart was given in the Division of Chemical Education, fall meeting of the American Chemical Society, Philadelphia, 1926. [For abstract of paper see J. CHEM. EDUC., 3, 953 (Aug., 1926).] A similar paper was presented by the author at the 1927 meeting of the South Dakota Academy of Science.

Geneva system. The hexose sugars that are assumed to have the —OH of the fifth carbon atom on the right side of the plane figure are arbitrarily called *d*- and those in which the —OH is assumed to be on the left side of the fifth carbon atom are arbitrarily called *l*-. This naming of the *d*- and *l*- forms does not in any sense refer to the dextro and levo rotatory power of these sugars; it is more of a means to distinguish between the mirror images of two similar isomers, *e. g.*, *d*-glucose has the structure (*3*)

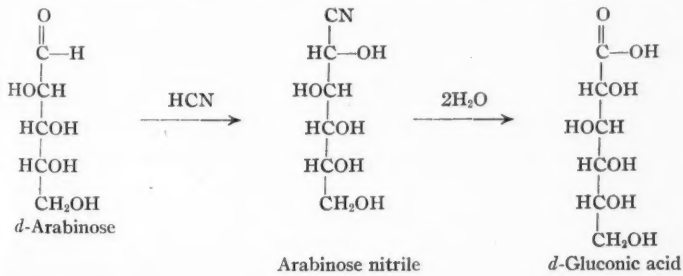


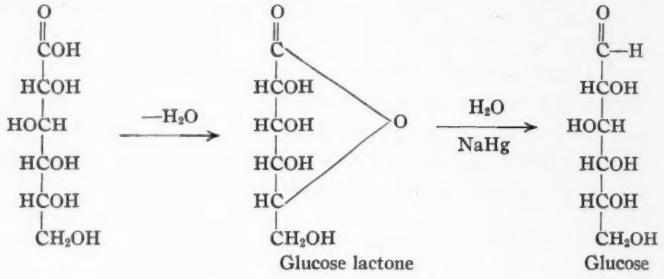
and *l*-glucose has the structure (*3*)



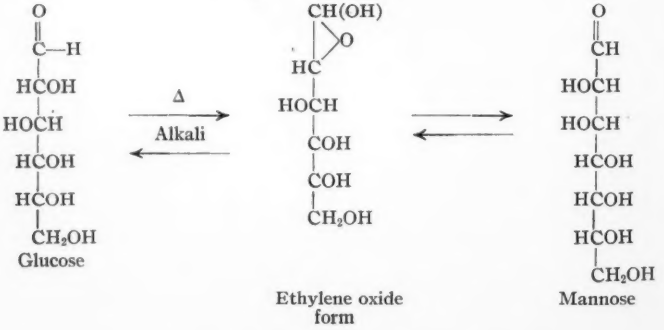
Explanation

Plate I shows the relationship that exists between the simple sugars. The reactions which indicate the chemical changes are designated by arrows that are numbered. In building up the carbon chain and passing





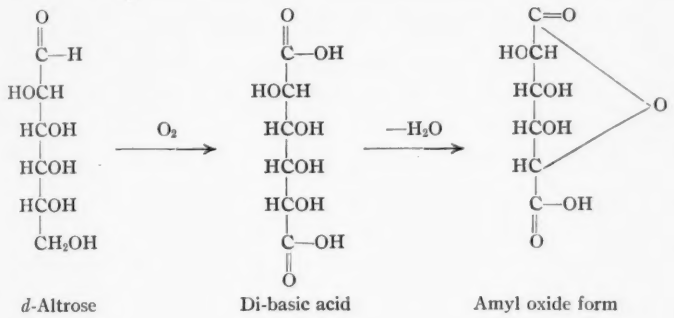
from a simple sugar to the next higher one, the Kiliana (*4*) reaction (arrow 1) is used. To illustrate the reaction, let us take a specific example. If to *d*-arabinose, HCN is added, the cyanhydrin is formed which may be hydrolyzed to the *d*-gluconic acid. The gluconic acid tends to lose water forming the lactone which is then reduced with sodium amalgam to glucose. This example is typical of all the reactions of 1. In passing from optical isomers (arrow 2) the reaction of Van Ekenstein is employed (*5*). The aldose, take glucose for example, is heated with various alkalis whereupon the enolic and then the ethylene oxide form is produced which rearranges to mannose; mannose being the nearest optical isomer of glucose. An equilibrium is of course reached from which the desired hexose may be isolated by fractional crystallization of the hydrozones.



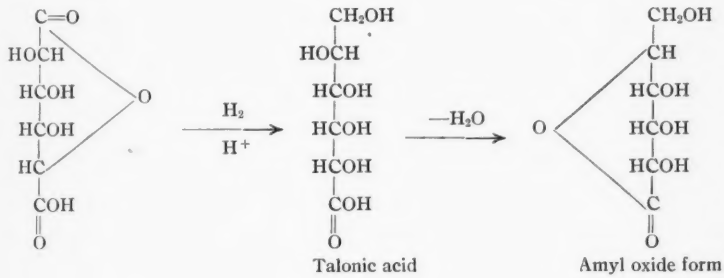
In the reactions relating to the exchanging of an aldehyde group for the end alcohol group (arrow 3) such as exists between *d*-altrose and *d*-talose, the altrose is first oxidized to the di-basic acid. This loses water to produce the amyl-oxide ring structure. Upon reduction the mono-basic acid of talose is formed. This again loses water to form the amyl-oxide ring of talose and, upon reduction, the talose is produced but exists probably in the lactone form.

THIS CHART WILL BE THE
SECOND CHART APPEARING
AT THE END OF THIS FILM

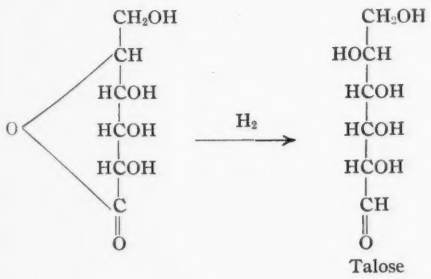
The relationship between the aldoses and ketoses is shown by the arrows numbered 4. An example of this is the passing from glucose to fructose. To glucose is added phenyl-hydrazine forming the glucosozone which



d-Altrose Di-basic acid Amyl oxide form



Talonic acid Amyl oxide form



Talose

upon hydrolysis and loss of water yields the glucozone. The glucozone upon reduction yields fructose (*6*).

The double arrows between closely related optical isomers show that the change may be effected either way.

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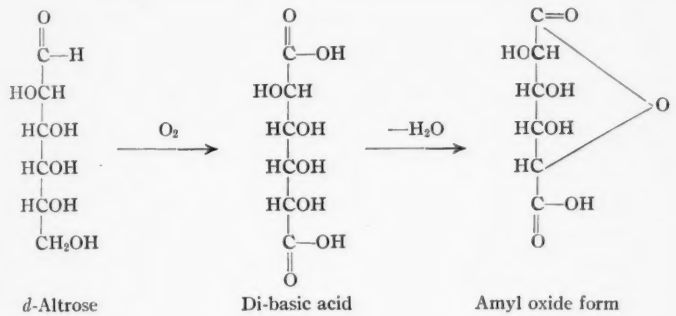

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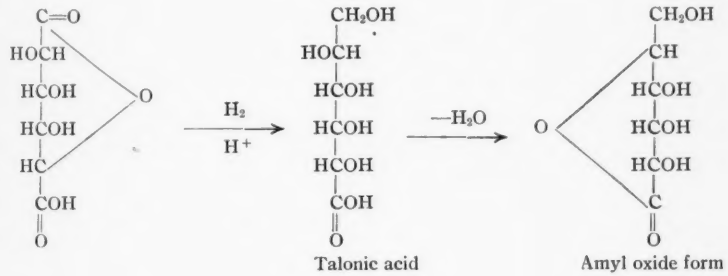
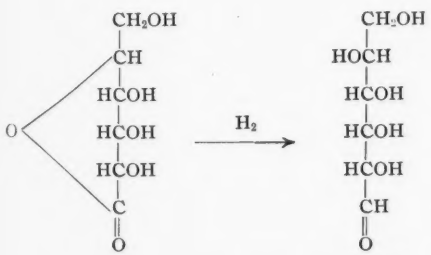


Talonic acid Amyl oxide form



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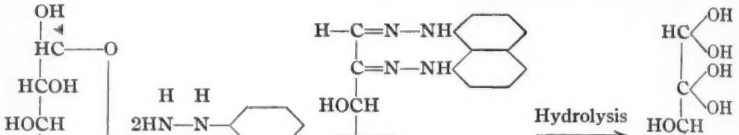

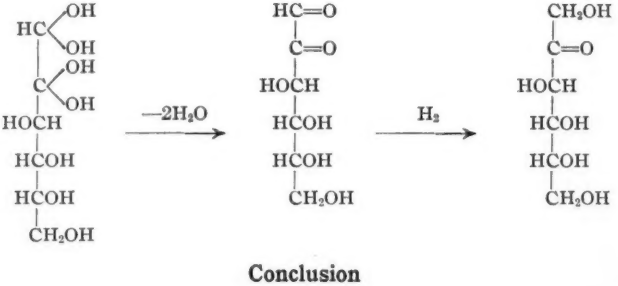

Conclusion

In the presentation of the chart the author has incorporated into it only the simpler structure of the carbohydrates and has left out the multiple forms possible if all the lactone structures were taken into consideration. According to Irvine (7) there are eleven possible structures for glucose alone; multiply the other homologs of this series by a proportional number of possible forms and it is evident that the construction of a relationship chart showing all these structures would be practically impossible. Therefore, it is hoped that the presentation of the chart as it is will facilitate the studying and teaching of the relationship among the simpler carbohydrates. More especially is it hoped that the chart may help to meet a need in the presentation of this phase of organic chemistry and that charts in general may come to have a greater part in the scientific studying and teaching of chemistry.

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(6) GORTNER, "Outlines of Biochemistry," John Wiley & Sons, Inc., **1929,** p. 505.
(7) IRVINE, "Progress in the Structural Study of Carbohydrates," *Chem. Reviews*, **4,** 203–29 (1927).

THE MEETING OF OSTWALD, ARRHENIUS, AND VAN'T HOFF*

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The recent publication of Ostwald's autobiography (*1*) adds materially to our information concerning the three founders of physical chemistry. I wish to confine myself, in this paper, to certain details dealing with the way in which a remarkable friendship sprang up among Ostwald, Arrhenius, and van't Hoff.

The year is 1884. Ostwald (1853–) is a professor at the Riga Polytechnik. He has become fairly well known as a worker and writer in the new field of chemical physics. In the month of June of that year he hears for the first time the name of "Arrhenius." He receives a reprint entitled "*Études sur la conductibilité des électrolytes*," and he finds that its author is Svante Arrhenius. On that day he has a bad toothache, also a daughter has been born to him. "That was too much!" The toothache soon disappeared; the daughter came into the world without much difficulty; but Arrhenius' paper...!

Klasing & Co., Berlin

A first reading led Ostwald to believe that the paper contained a lot of nonsense; but a second and third reading made him modify his view, particularly when he discovered in it a very rational explanation of the relationship of acids and bases—a subject to which Ostwald had devoted some time, but with partial success.

Having satisfied himself of the importance of this piece of research, Ostwald sent an abstract of the paper to the *Journal für praktische Chemie*, with a note to the effect that he, Ostwald, considered this paper by Arrhenius one of the most important within recent times. Fortunately for Arrhenius, and for the world, this abstract was published with very little delay.

So impressed was Ostwald with this paper by Arrhenius, that he decided to make the personal acquaintance of the young Swede. This became possible during the summer vacation of that year. Instead of going directly

* Read at the seventy-ninth meeting of the American Chemical Society, Division of History of Chemistry, April 8, 1930.

to Germany, as was his custom, Ostwald first went to Uppsala. Arrhenius awaited him at the station. As they had never met it was pre-arranged that Arrhenius should wave a reprint of his paper. "This personal meeting gave rise to a strong liking we developed for one another." This was the beginning of a friendship which lasted until the death of Arrhenius (1927).

The first evening in Uppsala was spent in a *Biergarten*. A number of Arrhenius' fellow students who happened to be there were very much impressed with the fact that a foreign professor, and an *ordentlicher* professor at that, had come to Sweden especially to meet Arrhenius. But if his fellow students were impressed, his professors were not. On the basis of his work, Arrhenius applied for the post of *Privat dozent*, and he was having difficulties getting the position. The professor of physics, Thalen, was so disagreeable that Arrhenius removed to Stockholm and there worked with Edlung (who, by the way, occupied the same quarters which Berzelius had occupied during the last few years of his life). The professor of chemistry at Uppsala, Cleve, was plainly surprised that Ostwald had come especially to Sweden to meet Arrhenius. "And so you think that in that beaker containing sodium chloride there are individual sodium atoms which swim hither and thither?" asked Cleve of Ostwald. Ostwald replied that such, to a certain extent, was the idea; whereupon Cleve shook his shoulders, pouted his lips, and plainly showed that he doubted the complete sanity of this Riga professor.

Years later, in an address delivered before the Chicago section of the American Chemical Society (*2*) Arrhenius referred very humorously to this same Cleve. "I came to my professor, Cleve, whom I admire very much, and I said, 'I have a new theory of electrical conductivity as a cause of chemical reactions.' He said, 'This is very interesting,' and then said, 'Goodbye!' He explained to me later that he knew very well that there are so many different theories formed, and that they are all almost certain to be wrong, for after a short time they disappear; and therefore by using the statistical manner of forming his ideas he concluded that my theory also would not exist long" (*3*).

Before Ostwald's departure from Sweden, arrangements were made to have Arrhenius join Ostwald in Riga at the very earliest moment, with the view to further work along the "new" lines; and Ostwald's recommendation while in Stockholm eventually persuaded the Swedish authorities to grant a traveling fellowship to Arrhenius. The Swedish scientist finally came to Riga in 1886; and for a time these two men worked in the same laboratory, though on somewhat different problems.

It was at this time that Ostwald procured a book called "*Études de Dynamique Chimique*," "that gave me more headaches than the paper by Arrhenius." The author, J. H. van't Hoff, was quite unknown to Ostwald,

though within the next few months there began an active correspondence between them. Arrhenius, however, the year before had already reviewed the book in glowing terms for the Uppsala *Nordisk Revy;* and this notice of the book came to the attention of van't Hoff, who immediately conceived a liking for the twenty-six-year-old reviewer. It was not, however, until 1888 that the two met; for then Arrhenius traveled to Amsterdam to work in van't Hoff's laboratory (*4*).

In 1887 the *Zeitschrift für physikalische Chemie* was founded by Ostwald, and van't Hoff became co-editor. In the first volume there appeared van't Hoff's celebrated paper on the function of osmotic pressure in the analogy between solutions and gases (*5*) and Arrhenius' equally celebrated paper on electrolytic dissociation (*6*). Ostwald and van't Hoff did not, however, meet until 1890, when both accepted an invitation to attend a meeting of the British Association. Ostwald joined van't Hoff in Amsterdam and they both proceeded to Leeds. At the station in Amsterdam Ostwald found awaiting him "a young, lean man, of average size—[van't Hoff (1852–1911) was a year older than Ostwald]—"with those typical long and drawn-out features of his compatriots." This was the beginning of an intimate friendship which lasted until van't Hoff's death in 1911.

Van't Hoff and Ostwald proceeded to Leeds to attend the British Association meeting. It was here that Ostwald and Ramsay met for the first time. Ramsay had translated van't Hoff's paper and had published it in the *Philosophical Magazine;* he was a convinced "ionist;" and he was bent upon seeing that the two continental visitors got "fair play," particularly since the anti-ionists were assembled in full force. A graphic account of the meeting has been left us by Professor Smithells (*7*) who describes the physicist, Fitzgerald, walking restlessly around the dinner table declaring, "I can't see where the energy comes from," and who tells us how Ramsay sprang to Ostwald's rescue—"his (Ostwald's) English at the time was imperfect and explosive."

Our three musketeers had but begun the fight for a recognition of the newer ideas in chemistry. There was much yet to do to overcome mental inertia, ultra-conservatism, and, be it added, intelligent criticism. But ultimately the victory went to the ionists. So complete, indeed, did the victory finally become that the much-prized Nobel prize went first to van't Hoff, then to Ostwald, and finally to Arrhenius.

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Toad Venom May Yield New Drugs for Medicine. The venom of toads, for centuries used in Europe as a source of poison and in China as a medicine, contains potent principles that resemble drugs in therapeutic use today and may provide medicine with new weapons against heart disease. Four kinds of chemical substances have been isolated in crystalline form from Ch'an Su, dried toad venom used as medicine in China for hundreds of years. The researches were conducted by Drs. H. Jensen and K. K. Chen of Johns Hopkins. Dr. Chen is a Chinese biochemist whose research on an old Chinese drug plant gave modern medicine the drug ephedrine which has come into wide use in the treatment of hay fever and colds.

In the river and lake regions of China is found a large toad which when irritated secretes a whitish, slimy venom from glands located behind the eyes. The Chinese have long used this dried venom in treating canker sores, sinus trouble, inflammations, toothache, and bleeding gums. The reason why the toad venom is effective for stopping bleeding and promoting drainage of infected sinuses was explained when Drs. Jensen and Chen isolated from the venom two principles which raised blood pressure, one of them identical with epinephrine or adrenaline, the principle of the suprarenal gland in animals.

But the poisonousness of toads is explained by the isolation of two toxic principles in the toad venom that have a pharmacological action quite similar to the familiar digitalis glucosides used in treating heart trouble. One of these, cinobufotoxin, as it is named in honor of its origin and toxicity, is so potent that one-thousandth of a gram would kill an ordinary cat. The other poison in the Chinese toad venom, cinobufagin, is not so powerful. These poisonous principles explain the cause of death of the husbands of marriage-weary Roman women who fed their mates toad lungs.

Other poisons of animal origin are snake venom and poisons from fish, scorpions, spiders, bees, ants, beetles, and other insects. In common with gland extracts such as thyroxin, adrenalin, pituitrin, and insulin, these poisons are toxic in large amounts but sometimes beneficial in small doses. Close chemical relations between toad poisons, digitalis, bile acids, cholesterol, ergosterol, the vitamin D substance, and perhaps the female sex hormone are suggested by Drs. Jensen and Chen and may guide their use in the treatment of disease.—*Science Service*

Oxygen Atoms Remove Oxygen from Compound. Removing oxygen from a chemical compound by shooting atoms of oxygen at it is the paradoxical result achieved in an experiment by Prof. W. H. Rodebush and W. A. Nichols, Jr., in the Laboratory of Physical Chemistry at the University of Illinois. The effect was produced with the chemical compound known as molybdenum trioxide. Removal of oxygen is called a "reducing action" by chemists. Atoms of hydrogen have a very great attraction for atoms of oxygen and pull them out of compounds to form molecules of water. Hitherto the effect has not been obtainable with oxygen atoms, and this is the first time that oxygen itself has been made to serve as a reducing agent. The experimenters say that with the molybdenum trioxide the effects of hydrogen and oxygen are identical.—*Science Service*

GRADE-SCHOOL METHODS AN ASSET TO THE CHEMISTRY TEACHER

BRUCE F. LAMONT, SENIOR HIGH SCHOOL, HAZLETON, PENNSYLVANIA

The most effective teaching is undoubtedly done in the grades. It is in this field that most of our educational research has been carried on. Most of the radical changes made in the methods of teaching have taken place in the grades. It was in this field that standardized tests were first perfected and utilized. Silent reading was introduced because it is only by this means that people read in life. Changes in the curriculum began in the elementary field, so grade teachers have been compelled to be on the alert and keep an ear to the ground, as new advances in their field are constantly being brought forward.

When many of us attended school we were carried through the intricacies of cube root, yet most of us have never had occasion to use it in actual life. Today children are drilled in the fundamental arithmetical operations with the aim to become skilful so that they later can cope with actual responsibilities.

In the field of reading, we can recall how we were taught to read, stand up reading aloud, with frequent admonitions to put more expression into our reading. Very few of us have had occasion to read aloud since. Investigators found that the better the oral reader the less the ability to comprehend. Undoubtedly the aim of all reading is comprehension. The result has been the introduction of silent reading into our elementary schools where the aim is the quick and accurate comprehension of what is read.

In our school days we were compelled to learn long lists of difficult words in our spelling classes. Words which we never used were learned and words we used daily were neglected. Investigations in the field of spelling resulted in the introduction of context spelling in the elementary grades. Fewer words are learned, but they are words which many investigations have shown to be most frequently used in actual life.

These are just a few of the changes which have taken place in the elementary field. Through a study of these modern elementary-school methods high-school chemistry teachers will acquire a philosophy of education which will broaden their outlook and make them better teachers. A sound philosophy is necessary for successful living, and so a philosophy of education is necessary for successful teaching. Chemistry teachers would do well to study the methods of teaching utilized in the elementary grades. By becoming familiar with the manner in which changes were brought about in the grade schools, high-school teachers will acquire an insight into the methods of research from which these changes have resulted. They will be better fitted to solve intelligently the problems met in their own classrooms. The solution of many problems of secondary education can only be reached by teachers who are actually in daily contact with the students.

A favorite maxim of the successful grade teacher is teach a thing in the way it is to be used. Grade-school teachers know that children can spell words in columns but miss them when writing sentences; some pupils recognize words in drill work but do not know them in reading. In arithmetic children know the arithmetical combinations but make errors in their use in actual problems. Grade-school teachers, therefore, aim to teach facts in the way in which they are to be used. Chemistry teachers are prone to neglect this fundamental principle of educational psychology.

It seems to be traditional with teachers in the secondary field that the aim of all education is the acquisition of facts. Factual material is crammed into the high-school pupil until he too believes this is why he is in school. The grade-school teacher can give the chemistry teacher an excellent lesson in this matter. By teaching a thing in the way it is to be used many of the facts we now teach lose their seeming importance.

The successful grade teacher of today has as her chief aim the preparation for life. Facts to her are only important to the extent to which they are useful in building correct habits and attitudes. Leadership, resourcefulness, neatness, politeness, tact, coöperation, responsibility, industry, and honesty are traits with which the elementary teacher is concerned. Chemistry instruction will better meet the needs of the pupils when teachers utilize the facts which they teach as a means of developing habits, attitudes, and ideals which will prepare students for life. Every high-school subject should contribute attitudes, habits, and ideals to the education of the pupil.

When facts are to be acquired the grade-school teacher is a master of the technic of drill. This is a fundamental weakness of all high-school instruction. Chemistry teachers frequently expect students to acquire a mastery of factual material without applying the laws of learning. Facts are presented and seldom drilled upon. Grade teachers have scientifically worked out the distribution of drill periods. This scientific distribution of drill periods at frequent intervals is lacking in the teaching of chemistry. Facts well drilled and aiming to develop civic, moral, and economic attitudes and ideals will follow as chemistry teachers study the methods used in the grades.

Many grade teachers have become expert in the teaching of silent reading. Here is a field for the high-school chemistry teacher. Little or nothing has been done in secondary education in the diagnosis of errors in reading of high-school subjects. Yet all high-school subjects are acquired largely through reading. Different reading abilities are required by different subjects. For instance, the study of science or mathematics requires a different reading ability than history. In many instances the writer has found that failure on the part of a high-school chemistry student has been due to the inability to comprehend what has been read because of

poor reading habits. In many instances the poor habits can be corrected by the use of proper remedial measures. High-school chemistry teachers will find improvement in their work through a study of the methods of silent reading as practiced in the grade schools.

Teachers in the elementary field know the value of a good assignment. They know that a study of any unit will fail in educational results unless it is preceded by a good assignment. Grade teachers aim to make their assignments definite and specific because they are dealing with immature minds. The assignment is motivated and made as a definite unit. The pupil is shown that his lesson is an answer to some definite problem. The teacher shows the pupil how to attack the new problem and then how to study it by studying with him. The teacher tells many interesting things about the new content which is not found in the textbook, and thus tries to overcome the pupil's reluctance for further reading. In the making and motivating of chemistry assignments the high-school teacher can learn much by a study of elementary-school methods.

In the grade schools the teacher individualizes instruction to an extent undreamed of by many high-school teachers. The elementary teacher is a friend and adviser to the pupil and in many instances in closer relationship to the child than the home. The successful grade teacher is serving as the best kind of a guidance counselor. By watching the grade teacher at work the high-school teacher will learn the methods of individualized instruction rather than mass teaching, and become better able to serve as guide and counselor to the pupils.

Much material is taught in the grades through dramatization and visualized instruction. Some high schools have made progress along this line, but much can yet be learned from the expert grade teacher. Chemistry is a subject which naturally lends itself to instruction through dramatization or visualized instruction. The secondary-school teacher must in the future make wider use of both dramatization and visualization.

In dealing with younger minds the elementary school teacher has been forced to practice modern educational methods. In many ways more expert teaching is done in this field than in the secondary schools, and chemistry teachers who make a study of elementary educational methods will improve themselves as teachers.

Rubber Explodes When Overworked. Strange is the behavior of ordinary, common rubber. Like water, it is non-compressible, but like a gas it stores as heat work done on it when it is strained and stressed. And rubber has been stressed so severely and so rapidly that it heated up and exploded, Walter C. Keys, of Detroit, Michigan, reported recently to the American Society for Testing Materials. Mr. Keys said that badly overloaded solid tires have been known to explode.—*Science Service*

AMERICAN CHEMICAL SOCIETY PRIZE ESSAY CONTESTS 1930-31

The Prize Essay Contest was inaugurated in 1923 by Mr. and Mrs. Francis P. Garvan and the American Chemical Society. Its fundamental purpose is to provide a means for students to acquire a better general appreciation of chemistry. Three separate contests are conducted by the Society with funds for administration and prizes provided by Mr. and Mrs. Garvan. These contests are open to (1) high-school students, (2) normal and teachers' college students, and (3) college freshmen.

The Prize Essay Contest is administered by a Committee appointed annually by the President of the American Chemical Society.

All communications about the contest should be sent to The Committee on Prize Essays, 654 Madison Avenue, New York City, N. Y.

General Subjects and a List of the Topics for Essays

I. General Subject—The Relation of Chemistry to Health and Disease

Topics for Freshman College and Normal School and Teachers' College Essays

1. Synthetic Medicines
2. Chemistry as an Aid to Public Health
3. The Contributions of Chemistry to Modern Surgery

Topics for High- and Secondary-School Essays

1. Chemistry and Public Sanitation
2. How Chemistry Protects the Public Health in My Town (or County, or State)
3. The Purification of Municipal Water

II. General Subject—The Relation of Chemistry to the Enrichment of Life

Topics for Freshman College and Normal School and Teachers' College Essays

1. Chemistry and Culture
2. How Chemistry Has Enriched Life in the Last Twenty-five Years
3. The Rôle of Chemistry in the Diffusion of Knowledge

Topics for High- and Secondary-School Essays

1. Chemistry and Labor-Saving Devices
2. How Chemistry May Contribute to Fruitful Enjoyment of Leisure
3. The Rôle of Chemistry in Music, Painting, Radio, and Motion Pictures

III. General Subject—The Relation of Chemistry to Agriculture or to Forestry

Topics for Freshman College and Normal School and Teachers' College Essays

1. Fertilizers and Agriculture
2. Pests in Agriculture, or in Forestry
3. Utilization of By-Products in Agriculture, or in Forestry

Topics for High- and Secondary-School Essays

1. Fertilizers in Agriculture
2. The Control of Insect Pests by Chemistry
3. What Chemistry Can Do to Utilize Waste Materials in Agriculture and Forestry

IV. General Subject—The Relation of Chemistry to National Defense

Topics for Freshman College and Normal School and Teachers' College Essays

1. Chemical Warfare—Offensive and Defensive
2. National Safety in Peace and War
3. Chemistry and Aviation

Topics for High- and Secondary-School Essays

1. The Place of Chemistry in National Preparedness
2. Chemistry and Aviation
3. Is the Use of Gas in Warfare Justifiable?

V. General Subject—The Relation of Chemistry to the Home

Topics for Freshman College and Normal School and Teachers' College Essays

1. Chemistry and Household Conveniences
2. Chemistry and Better Food
3. Sanitation in the Home

Topics for High- and Secondary-School Essays

1. How the Home Can Be Made More Livable through Chemistry
2. Chemistry and the Home Beautiful
3. Chemistry as an Aid in the Home

VI. General Subject—The Relation of Chemistry to the Development of an Industry or a Resource of the United States

Topics for Freshman College and Normal School and Teachers' College Essays

1. Chemistry the Salvager
2. The Relation of Chemistry to the Development of the Cellulose Industry
3. The Utilization of a Resource in a Major Chemical Industry in My Town (or State)

Topics for High- and Secondary-School Essays

1. A Chemical Industry in My Town (or State)
2. The Relation of Chemistry to (*a*) the Automobile, or (*b*) Cellulose, or (*c*) Building Materials, or (*d*) Alloys, or (*e*) Glass
3. Chemistry and the Utilization of Waste Products

Rules for the High- and Secondary-School Contest

1. Any student enrolled in any high or secondary school in the United States, who has not completed sufficient work to satisfy college entrance requirements, is eligible to enter the contest. Students who will graduate at mid-year may enter. It is not

necessary to be enrolled in any chemistry courses, or to have studied chemistry previously.

2. A contestant must confine his essay to one of the three topics listed under each general subject.

3. All essays submitted in this contest must be written under supervision such as is ordinarily given in usual written examinations in the school. No notes other than a skeleton outline may be used.

4. A contestant may submit only one essay.

5. The essay submitted should not exceed 2500 words. Any essay containing more than 2500 words will be rejected without reading.

6. The essay submitted should be typewritten, double-spaced, have wide margins and be on one side of paper $8^1/_2'' \times 11''$. The sheets must be numbered consecutively and securely fastened together. If typewriting facilities are not available, then legible handwritten essays should be substituted. Illegible essays will not be accepted.

7. A plain sealed envelope firmly attached to the essay must contain the full name of the contestant, the correct name and address of his school, his home address, and the exact number of words in his essay. No other identification of the writer of the essay must appear, either on the essay itself or the envelope.

8. All direct quotations must be enclosed in quotation marks and due credit must be given to sources of reference. Lengthy quotations must not be included.

9. Exhibits or illustrations must not be made a part of, or accompany, an essay.

10. Duplicates of essays submitted in former contests will not be accepted.

11. Essay must be forwarded by the principal or teacher with the statement that it was written under supervision and is the original work of the student and must be received at the office of the Chairman of the State Awards Committee on or before March 1, 1931.

12. By the act of entering an essay in the contest, the writer gives to the Committee on Prize Essays of the American Chemical Society full right to its permanent possession, publication rights, etc.

Rules for the Normal School and Teachers' College Contest and for the College Freshman Contest

Rules 2 to 10 inclusive are identical for all three contests. For Rule 1 substitute the appropriate paragraph below:

1. For the purpose of this contest a normal school or teachers' college student shall be a regularly enrolled student of a school such as listed in Section XVI of the Educational Directory of the Bureau of Education, United States Department of the Interior.

1. For the purpose of this contest an undergraduate Freshman shall be a student who has satisfied college entrance requirements, is enrolled in such an institution, and is continuing the regular work of a first-year collegiate grade.

For Rules 11 and 12 substitute Rules 11, 12, and 13 as follows:

11. Essay must be forwarded by the professor in charge with the statement that it was written under supervision and is the original work of the student.

12. Essays must be in the hands of the Secretary, Committee on Prize Essays, American Chemical Society, 654 Madison Avenue, New York City, not later than March 1, 1931.

13. By the act of entering an essay in the contest, the writer gives to the Committee on Prize Essays of the American Chemical Society full right to its permanent possession, publication rights, etc.

PRIZES

High-school prizes are awarded in two contests—State and National.

In each State Contest twelve (12) prizes are awarded, two for each general subject, as given in Rule 2. The first prize in each subject is a $20 gold piece, a first prize certificate, and entrance of the essay in the National Contest. The second prize in each subject is a book on chemistry, a second prize certificate, and entrance of the essay in the National Contest.

The National Prizes are six four-year scholarships in any recognized college or university in the United States. Each scholarship provides tuition fees and $500 in cash annually.

Six prizes of $500, six prizes of $300, and six prizes of $200 will be awarded to students of normal schools and teachers' colleges in the United States who write the first, second, and third best essays, respectively, on topics under the six general subjects of the contest.

Six prizes of $500, six prizes of $300, and six prizes of $200, will be awarded to freshmen attending colleges and universities in the United States who write the first, second, and third best essays, respectively, on topics listed under the six general subjects of the contest.

Inquiries for further information about the contests and requests for bibliographies should be addressed to Paul Smith, Secretary, 654 Madison Avenue, New York City.

Common Tap Water Stops Ultra-Violet Radiations. Pure water, containing no mineral salts in solution, transmits ultra-violet light fairly well, but a little dissolved mineral makes a thin layer of water much less transparent to these invisible radiations. How little, Dr. Charles D. Hodgman of the Case School of Applied Science, Cleveland, Ohio, recently told members of the American Physical Society. He found that a layer less than an inch thick of common lake water, taken from Lake Erie, and containing no more mineral than most city water, stops about a quarter of the longer wave ultra-violet rays and nearly nine-tenths of the short-wave rays.—*Science Service*

Sugar of Germ Cells May Be Most Important Part. The different sugars of germ cells are probably among the most important chemical substances concerned with the vital processes of the cells, Prof. Treat B. Johnson of Yale University said before the recent meeting of the National Tuberculosis Association at Memphis, Tennessee. In the Yale laboratories, tuberculosis germs by the pound have been analyzed chemically and found to contain among other things poisonous sugars. The sugars of the bacterial cells exist in very complex forms. The existence of these complex, highly poisonous sugars appears to be characteristic of germ cells in general, and is not necessarily characteristic of the tuberculosis germs alone. When considering the question of immunity to diseases, the proteins of the cells have been given chief attention. Prof. Johnson suggested that the sugar of the cell must now be taken into consideration as well.—*Science Service*

SOURCE MATERIAL FOR PRIZE ESSAY CONTESTS

GEORGE W. BENNETT, GROVE CITY COLLEGE, GROVE CITY, PENNSYLVANIA

The problem of obtaining suitable material for assigned readings in general chemistry, for the science or chemistry club programs, or for prize essay contests often proves most troublesome. The first- or second-year college student is not usually in a sufficiently advanced stage of progress in chemistry to be referred to the technical journals with either pleasure or profit, and even the third- and fourth-year students have some trouble in using what technical journals are available. This situation in recent years has been alleviated by the publications of The Chemical Foundation and by the JOURNAL OF CHEMICAL EDUCATION. There is, however, a rather extensive literature of chemistry appearing in contemporary non-technical magazines that is well adapted to the needs of undergraduate students for general purposes. These articles are written in language for the layman, but are largely authoritative for they are often written by the most eminent chemists of our day. A surprisingly large number of people do not know that the periodical literature is well indexed, but it is, and an abundance of material is available in the smallest library.

There is no one index to all the periodical literature, but rather a number of indexes, each of which serves a particular purpose. Of these indexes the one which has the greatest utility for the topic suggested is the "Readers' Guide to Periodical Literature."[1] This guide is found in most libraries. The "Readers' Guide" appears in four-, three-, and later two-year summations, with annual, semi-annual, and monthly summations to bring the index up to date from 1900 inclusive.

For this period over 1000 titles are listed under the headings "chemical," "chemistry," and "chemists," and there is a multitude of related topics such as "colloids," "fuels," "metallurgy," etc. The range of topics is great. Information can be found, for instance, on every topic suggested as desirable for a course in pandemic chemistry (*1*), or for The American Chemical Society prize essay subjects (*2*). A list of names of authors of these articles would be an international roll of honor of great chemists and physicists, and would include more than one Nobel prize winner.

An item of importance for the small library not to be overlooked in passing is that the magazines indexed are fairly common and include such sources as *Current History, Current Opinion, Literary Digest, Popular Mechanics, Radio Broadcast, Science, Scientific American, Scientific Monthly,* and other similar magazines.

Of less utility, perhaps, is the "International Index to Periodicals."[1] This index covers a different series of magazines from that of the Readers' Guide. The articles indexed are more technical in subject matter, but there is the novel advantage of articles in French, German, and English, if the appropriate magazines are available.

[1] Published by H. W. Wilson Co., New York City.

The "Annual Magazine Subject-Index,"[2] appears annually since 1907 and covers some 160 magazines. Its field is generally inclusive, supplementing the "Readers' Guide" and the "International Index," but it does not list much under "chemistry."

The "Industrial Arts Index,"[1] is more technical than either the "Readers' Guide" or the "International Index," indexing articles in some 250 technical and trade journals. The field is better covered, of course, by *Chemical Abstracts*. This index appeared in annual volumes from 1913 to 1917, and in two-year cumulations since that time. It also cites French, German, and English sources.

The "Agricultural Index,"[1] is a mine of information on chemistry in agriculture, but it is more difficult to use because the titles are not indexed, of course, with chemistry as a paramount interest. It indexes 150 agricultural journals, experiment station literature, and literature of the agricultural departments of many countries. References are to articles in French, German, Italian, Spanish, and English. This index appears in three-year cumulations beginning with 1916.

"Poole's Index to the Periodical Literature" was the first of such indexes.[3] The articles indexed begin with 1802 and conclude with 1907. A variable number of magazines were indexed in that period. The first volume covering the period 1802–1881 has an extensive list of topics on chemistry, but they would now be practically of historical interest only.

When it comes to books the library card catalog probably will serve the student's interests best, but the "United States Catalog"[1] lists author, subject, and title indexes of all books in print. There are seven pages devoted to "chemistry" which covers about 1000 books. There are also separate sections for allotropy, alloys, atomic theory, phase rule, solutions, and numerous similar topics. The "Cumulative Book Index," by the same publishers, supplements the United States Catalog annually.

It is unlikely that all these indexes will be found at one time in all libraries, but if one or more of them is available, as well as a reasonable range of current magazines, then a large amount of understandable, authoritative, and helpful material for assigned readings, club programs, or the essay contests may be readily found in what sometimes appears to be a welter of periodical literature.

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(*2*) "The A. C. S. Prize Essay Contest," J. CHEM. EDUC., **6**, 1805–6 (Oct., 1929).

[2] Published by F. W. Faxon Co., Boston, Mass.

[3] It is published by Houghton, Mifflin, and Co., Boston and New York, who also published an abridged edition of this famous index.

THE CHEMICAL MAN

HELLMUT BAUER, HIRAM COLLEGE, HIRAM, OHIO

It has been the custom in the past years at Hiram College to stage an annual scientific exhibit, in which working models illustrating various industries and representing the demonstrational proof of scientific principles are shown. In the department of chemistry a classmate, Vernon Webster, and I had occasion to present an exhibit on chemistry in medicine. Since we wished to depart from the usual nature of an exhibit on this subject, which consists of a host of bottled medicines and numerous posters, we made an attempt to show the chemistry involved in the main functions of the human body. The resulting model was dubbed the "chemical man" of the exhibit. (See illustration on page 2711.)

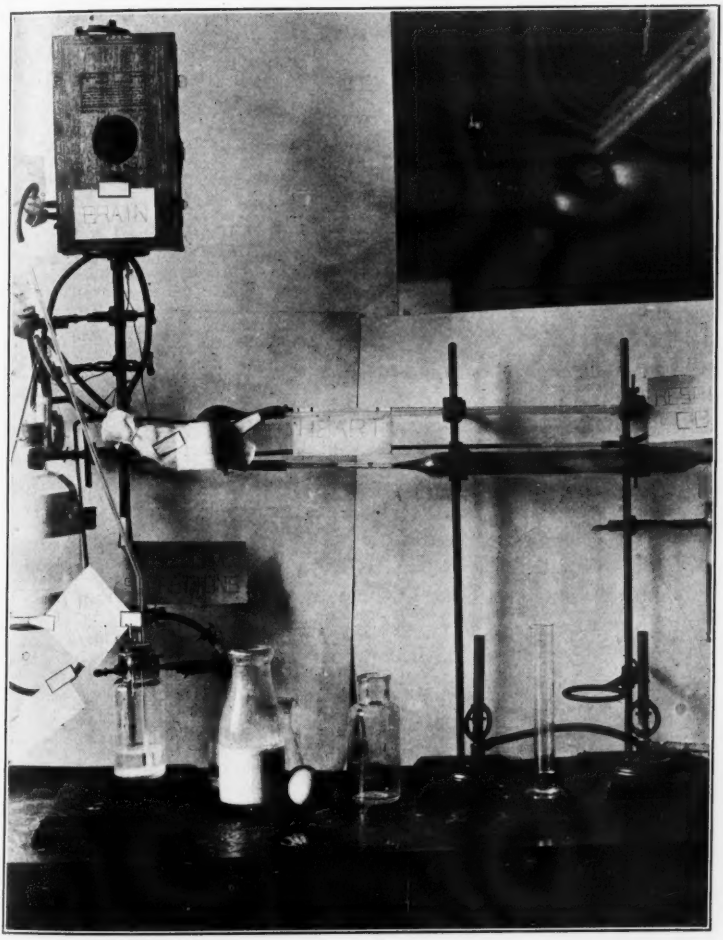
Owing to the technical difficulties and our limited knowledge of the chemistry of the human body, we confined ourselves to four systems: the circulatory, respiratory, digestive, and nervous systems. Consequently, our "chemical man" could eat and breathe; had a heart that would beat; and was sensitive to touch and to sound.

The circulatory system consisted of a heart which was operated by an atomizer bulb; and the blood stream passed from the auricles to the ventricles, making a circuit to the principal organs incorporated in the model. To avoid a backward flow of the blood with contraction of the heart, valves were inserted into the arteries of the blood stream. The blood itself was nothing more than a solution of ferric thiocyanate, made by adding ferric chloride to a solution of ammonium thiocyanate. The deep red color of the resulting solution proved to be a very satisfactory imitation of that of blood.

In the respiratory system the absorption of oxygen and elimination of carbon dioxide, which is produced by the burning of the tissues in the human body, were demonstrated. Air was drawn in by means of a suction pump attached to one tube through which the used air was drawn out. In a wide piece of hard glass tubing, finely divided carbon was burned to represent the oxidation of the carbon in the human tissues. The resulting carbon dioxide was passed through a solution of clear lime water, which was turned milky by the calcium carbonate formed.

The brain of the chemical man consisted of a sound box made by taking the bottom out of a cigar box and stretching a piece of paper over this opening. In the center of this paper was inserted an electric wire, and close to the wire the other end of the circuit comprising the sound system was secured; this was adjusted so finely that sound vibrations closed the circuit and caused the light of a lamp, which was connected to the circuit, to fluctuate with the intensity of the sound waves. The touch system was nothing more than a circuit which was closed at a certain point by grasping the "arm" of the model.

The greatest difficulties were encountered in the digestive system, where the chemical action involved was much more complex and not nearly so apparent. To show that certain changes occur, we made tests upon the



"THE CHEMICAL MAN" ASSEMBLED

food after some time of "digestion." The gastric juice contained highly diluted muriatic acid, pepsin, and rennet, and the food consisted of bread, milk, and eggs. A Fehling's test for sugar was made to show that the muriatic acid had hydrolyzed the starch to sugar; the souring of milk was physically apparent, but nevertheless a test for lactic acid was made by the action of ether on the substance to be tested, subsequent separation in a separatory funnel and the addition of ferric chloride to obtain a greenish yellow solution. A test for peptones by the action of pepsin was impossible because of the length and tediousness of the procedure.

NEW LABORATORY PREPARATIONS FOR THE COURSE IN ORGANIC CHEMISTRY. II.* DECANE FROM *N*-AMYL BROMIDE BY THE WURTZ REACTION

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An important organic synthesis is that of the formation of higher aliphatic, mixed aliphatic-aromatic, or higher aromatic hydrocarbons by the reaction discovered independently by Wurtz (*1*) for the aliphatic compounds and by Fittig (*2*) for the mixed aliphatic-aromatic compounds. Student preparations, illustrative of this reaction, ordinarily require the presence of dry solvent ether. This necessitates operations involving the drying of ether; in addition, the presence of ether in the reaction mixture slows up the reaction so that one laboratory period is used in carrying on the condensation and much of the second period in recovering the product from the reaction mixture.

The author feels that there is just as much to be gained by a shorter preparation and is giving the laboratory details for the preparation of decane from *n*-amyl bromide as an illustration of such a preparation. The method for preparing the alkyl bromides by the action of concentrated sulfuric acid and sodium bromide on the alcohol, as outlined in "Organic Syntheses, Vol. I," has been modified and directions are also given for this reaction as a student preparation in place of the more common preparations of ethyl or butyl bromides.

Amyl Bromides

The alcohol used as a starting point in the synthesis is the *n*-amyl alcohol furnished by the Sharples Solvents Corporation. The material which is 80–90% *n*-amyl alcohol and contains as its chief impurity iso-amyl alcohol (3-methyl butanol-1), is satisfactory for general student use although if it is desired to prepare a product of higher purity, this may be accomplished by careful fractionation. The alcohol as used in the following work boiled between 136–136.5°.

The directions for a class for the preparation of amyl bromide (*3*) are as follows:

Set up a 500-cc., round-bottom, short-neck flask, condenser, and addition tube, with the condenser in the reflux position on the slanting arm of the addition tube. Fit a dropping funnel with a rubber stopper of such size as will be taken by the upright arm of the addition tube. Before putting in the dropping funnel add 27 cc. of water to the flask and then follow this by stirring in 31 grams (0.3 mol) of finely powdered sodium bromide. This must be carried out as directed or the bromide will form a hard cake. Twenty-two grams (0.25 mol) of *n*-amyl alcohol are next added. Now connect the dropping funnel and condenser and run in through the dropping funnel, shaking the contents of the flask occasionally, 40 grams (about 0.4 mol) of concentrated sulfuric

* For I, see J. CHEM. EDUC., **7**, 856–8 (Apr., 1930).

† Now located at The Institute of Paper Chemistry, Appleton, Wisconsin.

acid. Reflux the mixture for two hours, set the condenser for distillation, and distil until the distillate is free from oil. Separate this, wash with water, then with 20 grams of cold concentrated sulfuric acid and finally with a 5% sodium carbonate solution. Dry the amyl bromide over calcium chloride and distil, collecting the fraction between 126–129° as amyl bromide. The yield will be about 60% of the theoretical.

Decane

The mechanism of the Wurtz reaction has been very thoroughly considered by Bachman and Clarke (*4*). The influence of operating conditions in the preparation of octane has also been considered by Lewis, Hendricks, and Yohe (*5*). These papers should be consulted for details. Two reaction mechanisms are used to account for the products of a Wurtz condensation. One involves the formation of the sodium alkyl through the action of sodium on the alkyl halide. This condenses with the remaining halide to form the hydrocarbon (I).

$$\text{(I)}\quad \begin{aligned} \text{R—X} + 2\text{Na} &\longrightarrow \text{R—Na} + \text{NaX} \\ \text{R—X} + \text{RNa} &\longrightarrow \text{R—R} + \text{NaX} \end{aligned}$$

In the second a free alkyl radical is formed by the action of sodium on the halide; two free alkyl radicals then may combine to form the hydrocarbon (II).

$$\text{(II)}\quad \begin{aligned} \text{R—X} + \text{Na} &\longrightarrow \text{R}' + \text{NaX} \\ \text{R}' + \text{R}' &\longrightarrow \text{R—R} \end{aligned}$$

The reaction between *n*-butyl bromide and sodium is too violent for general student use in the absence of solvent ether; *n*-amyl bromide will work rather well in the absence of the ether—hence it is possible to carry out the greater part of this preparation within one laboratory period. With *n*-amyl bromide the principal product is decane; in the presence of an excess of sodium very little unchanged amyl bromide remains and the fractionation proves to be rather simple.

The directions for a class for the preparation of decane are as follows:

Set up a 500-cc. round-bottom, short-necked flask, condenser, and addition tube, with the condenser in the reflux position in the slanting arm of the addition tube. Select a tight-fitting rubber stopper for closing the straight arm of the addition tube. Now run in 30 grams (0.2 mol) of amyl bromide and then through the straight arm add slowly and in small pieces 7 grams (0.3 mol) of sodium. The sodium is added fast enough to keep the mixture refluxing; the neck of the addition tube is stoppered after each addition of sodium. Toward the end of the reaction the mixture becomes a pasty blue mass. After the sodium has all been added and the reaction has moderated, *cautiously* warm to a reflux temperature and maintain at this point for 15 minutes additional. Now cool the flask in a water-bath and run in 150 cc. of ether; this should cover the reaction mass. Replace the stopper in the upright arm of the addition tube with a 60-cc. dropping funnel and slowly add water a drop or two at a time to destroy the sodium. When the reaction is complete, the sodium will have disappeared and the sodium bromide will be completely dissolved in the lower aqueous layer. The decane is found in the top ethereal layer. Separate this, dry with calcium chloride and fraction-

ate, the portion distilling between 160–175° is collected as decane. On redistillation a product boiling between 170–174° (cor.) is recovered. The yield is about 55–65% based on amyl bromide.

Observations

1. The first piece of sodium added will become blue, begin to swell and then as the temperature of reaction causes it to melt will appear to erupt from within very much in the manner of popcorn. As soon as this has happened, it is safe to add the next piece of sodium. These should be no larger than a small pea.

2. The blue color (possibly due to an unstable modification of sodium bromide) remains throughout the condensation but rapidly disappears as water is added.

3. If water is not added too rapidly, this method for destroying sodium is safe. The senior author has used it on reacting masses in 5-liter flasks and considers it much more satisfactory for general use and much safer than the common practice of distilling from the reaction mass. Under some conditions this latter procedure is extremely hazardous.

4. The decane thus prepared, while containing small amounts of 2,7-dimethyl octane as an impurity, is satisfactory for many purposes, such as a material for use in testing properties of aliphatic hydrocarbons and as one component for a study of certain types of boiling-point curves.

This method of preparation for decane has the advantages that no dried ether is required as a solvent and the reaction may be completed in one laboratory period.

* * * * *

The author wishes to acknowledge the advice and help of the Sharples Solvents Corporation in connection with the preparation of a satisfactory n-amyl alcohol.

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(2) TOLLENS and FITTIG, *ibid.*, **131**, 3031 (1864).
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Indian Hemp, Common Weed, Possible Source of Rubber. A victim of disparagement for many years, Indian hemp, a common weed, has at last been given a place in the society of plants of economic value. Scientific research, according to the *Missouri Botanical Garden Bulletin*, has revealed that the weed, known scientifically as *Apocynum*, has rich rubber content. "One of the most significant factors concerning the study of the latex of *Apocynum*," says the *Bulletin*, "is that the rubber content increases to a large extent with drought and infertility of the soil."—*Science Service*

APPROXIMATE MOLECULAR WEIGHTS FROM THE BOILING-POINT RISE: A LABORATORY EXPERIMENT IN ELEMENTARY CHEMISTRY*

ARTHUR ROSE† AND R. D. BILLINGER, LEHIGH UNIVERSITY, BETHLEHEM, PENNSYLVANIA

This experiment was designed to give students first-hand experience with such topics as the effect of a solute on the boiling point of a liquid and the calculation of approximate molecular weights. The problem could be presented to the students in the following form: This compound has been found on analysis to contain $x\%$ C and $y\%$ H. Calculate the empirical formula and by means of boiling-point determinations find the approximate molecular weight of the compound and write the molecular formula. It is well to emphasize at the start that the method gives only approximate molecular weights and is used to determine which multiple of the formula weight is the exact molecular weight.

In a general way this experiment is similar to and illustrates the same principles as freezing-point experiments. However the latter have certain disadvantages when attempted in an elementary laboratory. On an ordinary thermometer the zero mark is always near the bulb. As a result it is difficult to get accurate readings in a freezing-point experiment since the bulb and lower part of the scale are inside the apparatus and often under the solution. Supercooling effects are impossible to prevent and these confuse the elementary student. The use of stirrers is essential and this complicates the apparatus. Finally the melting ice and salt mixtures are invariably spilled over the desk and result in a messy laboratory.

All these disadvantages are overcome by use of the following boiling-point experiment. The apparatus and procedure are so simple that no special supplies are necessary and yet the experiment is a test of the student's ability to set up apparatus and get results in the laboratory. The character of the experiment and the precautions to be observed are best indicated by stating the directions actually given to a class in general chemistry.

Determination of the Boiling Point of Pure Carbon Tetrachloride

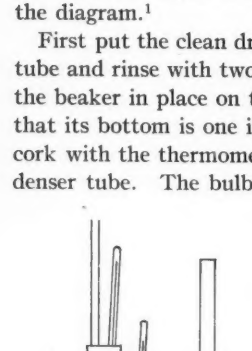
Each student will need the following apparatus: Bunsen burner, ring stand, iron ring, wire gauze, clamp, 400 cc. beaker, clean *dry* 7-inch test tube with two hole cork to fit, 2-foot length of glass tubing, 2 ordinary 0–110°C. range thermometers and 20 two-inch lengths of capillary tubing (1 mm. inside diameter) sealed at one end only. In order to determine the

* Essentially this same paper was presented before the Division of Chemical Education of the A. C. S. at the Atlanta meeting, April, 1930.

† Present address is Pennsylvania State College, State College, Penna.

boiling point of pure carbon tetrachloride, set up the apparatus as shown in the diagram.[1]

First put the clean dry capillary tubes[2] (open end down) in the dry test tube and rinse with two portions of pure carbon tetrachloride. Then put the beaker in place on the ring stand and clamp the test tube in place so that its bottom is one inch from the bottom of the beaker. Next fit the cork with the thermometer and the glass tubing, which is to act as a condenser tube. The bulb of the thermometer should be one inch from the bottom of the test tube when the stopper is put in place. When all is adjusted pour 12 cc. of pure carbon tetrachloride into the test tube, put stopper in place, and nearly fill the beaker with tap water. Finally put the second thermometer in place so that it will record the temperature of the water.



Heat the beaker with full Bunsen flame until the water reaches 80–85°C. Then remove the flame while the temperature gradually rises. During the remainder of the determination use a small Bunsen flame whenever the water temperature drops below 88°, but stop heating as soon as the temperature goes above this. In this way the temperature of the water is kept between 85° and 90°.

As soon as the temperature of the water has been adjusted, begin to take readings on the thermometer in the test tube. Read every minute to tenths of a degree and record all the readings and corresponding times. Continue to take readings until the temperature remains practically constant for a five-minute period (variation should be less than three-tenths of a degree). Average the five values and record this temperature as the boiling point of the carbon tetrachloride.

Approximate Molecular Weight of Naphthalene from Boiling-Point Rise

Prepare a naphthalene solution by dissolving about 5 g. of naphthalene (weighed to tenths of a gram) in 25 cc. of carbon tetrachloride accurately

[1] It was found helpful to exhibit a model apparatus in the laboratory so that all students could see just what was necessary. Each student's apparatus was then inspected, approved, and graded before he actually began the determination.

[2] Capillary tubes were found much superior to glass beads in preventing superheating and variation in boiling point.

measured from a graduated cylinder. Dismantle the test tube part of the boiling-point apparatus and pour out the carbon tetrachloride. Rinse the capillary tubes and test tube with two 5-cc. portions of the naphthalene solution just prepared. Then pour 12 cc. of the solution into the test tube and re-assemble the apparatus. Determine the boiling point of this solution exactly as was done for pure carbon tetrachloride.[3]

The difference in the boiling points of carbon tetrachloride and of the solution is the boiling-point rise for the solution. From this value and the molar-boiling-point elevation for carbon tetrachloride calculate the molarity of the naphthalene solution and the approximate molecular weight of naphthalene.

Discussion

The same procedure can be used for other boiling-point determinations, in each case keeping the heating liquid[4] about ten degrees above the temperature of the boiling solution in the test tube. It is necessary to use rather concentrated solutions in order to get sufficient elevation for reasonably accurate observations with an ordinary thermometer. The solution mentioned in the above directions is about molar.

It is easy to think of extending the method of this experiment to solutions of ionogens to illustrate and measure ionization. However, water is an unsatisfactory solvent because of its unusually small boiling-point constant. That it is such a common solvent and the only available ionizing solvent should probably outweigh the above disadvantages but it is difficult to get results showing an average error of less than 10 to 15% without introduction of special apparatus.

Carbon tetrachloride has a considerable advantage over water and other solvents because it has an unusually large boiling-point constant (water 0.52, benzene 2.56, carbon tetrachloride 4.85) and because of its non-inflammability and low boiling point.

Using the naphthalene–carbon tetrachloride combination, the better students can be expected to get results within two or three units of the correct molecular weight ($C_{10}H_8 = 128$), while the average error for the class should be less than 5%. Since the experiment involves some concentra-

[3] The following alternative procedure can be used in preparing the naphthalene solution: Remove the test tube from its clamp and cool under the tap. When the carbon tetrachloride has cooled, remove the cork, and add 2 g. of naphthalene (weighed accurately to tenths of a gram) to the carbon tetrachloride. Then re-assemble the apparatus and determine the boiling point of the solution. This method avoids the error due to evaporation of solvent during rinsing of the test tube, but the error in measuring the smaller amounts of carbon tetrachloride and naphthalene becomes relatively more important.

[4] For solutions having a boiling point greater than 100°C., a bath of crude glycerin is probably the most satisfactory heating liquid for general use in elementary laboratory work.

tion and close observation, a few students will get very poor results or even fail to finish in the time allotted. For instance, in a section of seventeen students one student did not finish, another obtained a value of 160, while seven students had values between 123 and 133. The average error for the section was 3.1%.

Although neither naphthalene nor carbon tetrachloride are familiar substances to the ordinary elementary student, a mention of their connection with moth balls and dry cleaning, respectively, should establish helpful associations in connection with the experiment.

Rules for Reading. How and why should books be read? It is to be feared that far too many read books merely to kill time, or else for frothy entertainment. Even informative books are often hastily skimmed over to pick out that which interests, rather than to absorb and retain the information which the author seeks to impart. According to Dr. Rollo L. Lyman of the University of Chicago, the following rules should be observed in order to get the largest amount of good from reading. Dr. Lyman states that a careful reader:

1. Reads with a definite purpose, a problem, in mind.
2. Grasps the author's point of view and central theme.
3. Lays hold of the order and arrangement of the author's ideas.
4. Pauses occasionally for summarizing and repeating.
5. Constantly asks questions of his reading.
6. Continually supplements from his own mental stock.
7. Evaluates the worth of what he reads.
8. Varies the rate of his progress through the reading.
9. Ties up what he reads with problems of his own.—*Kalends* of the Waverly Press

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Removing Metal Scale. After years of experimentation, a firm in New England has perfected a method of removal of scale resulting from heat-treating and hardening operations on metals, not only from flat surfaces but from such intricate machine parts as gears, shafts, etc., as well as from cutting tools, such as drills, taps, dies, cutters, and reamers. The scale is removed without in any way injuring the surface structure of the steel or metal part.

The process is an electrochemical one, the descaling action being brought about by the generation of hydrogen on the work, at the same time protecting the work from hydrogen embrittlement or pitting by coating the cleaned work by depositing a metal on it. This coating remains on the work, if it will not interfere with subsequent operations. It can easily be removed electrolytically if found to be undesirable.

This process makes it possible to do away with the hand work formerly necessary, like filing, sand-blasting, scraping, and scratch brushing, and thus greatly reduces the labor cost. Further study is being made of the adaptation of this process to the special fields in the metal industry. It is expected that it will have very wide application.

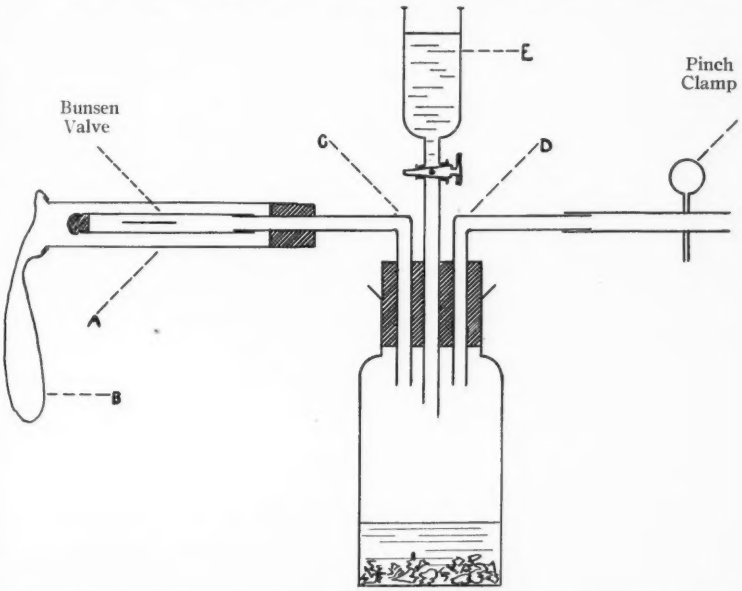
The process is said to be so simple that only a small installation is required, embracing a motor generator for the current and tanks in which the treatment is given.—*Ind. Bull., Arthur D. Little, Inc.*

HYDROGEN BALLOONS

GUY M. LISK, NORTHWESTERN STATE TEACHERS' COLLEGE, ALVA, OKLAHOMA

Ordinarily no course in first-year chemistry is considered complete unless some rubber balloons have been filled with hydrogen and "sent up." To avoid the trouble of generating hydrogen, and first filling a large rubber bag or other receptacle and then forcing the gas into the balloon, the device described herewith has been found quite satisfactory.

When the balloon is filled, or more acid is to be admitted into the generator, the pinch clamp is opened. It is at this point that the Bunsen valve functions by preventing the escape of the gas already in the balloon.



The tube *A* consists of a test tube from which the closed end has been removed. The flange on the open end holds the balloon tightly so that no string is needed.

A T-tube may be substituted for tubes *C* and *D*, and a 2-hole cork used. Or, a T-tube with a 2-way stopcock in it does away with the pinch clamp. Further, using a 3-hole cork as shown in the drawing, substituting a T-tube with a 2-way stopcock for tube *C*, and using *two* Bunsen valves, two balloons may be attached at the same time, and when one is filled the gas may be easily switched to the other, thus saving time and gas.

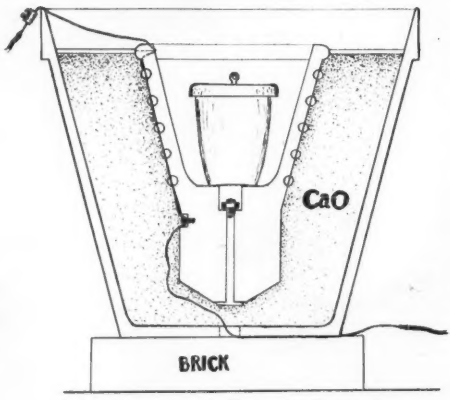
If desired, a calcium chloride drying tube may be placed between tube *C* and the Bunsen valve, but the balloon "goes up" without drying the gas.

A SMALL LABORATORY ELECTRIC FURNACE

EUGENE F. COLEMAN, DORMONT HIGH SCHOOL, DORMONT, PENNSYLVANIA

The heating of substances in small crucibles to temperatures in excess of 1000°C. is quite often necessary in chemical laboratories. One of the most convenient methods of doing so is to use a resistance electric furnace. An efficient little furnace, whose great advantages are ease and economy of construction, has been built by the author and will be described here.

A *conical* heating element of the type used in household electric heaters is procured at any electric appliance store. The thin copper screw around the base of the element is removed by tearing with a pair of pliers. The small bolt recessed into the side of the base, which will now be seen, is one of the terminals. A bare No. 14 copper wire should be securely twisted, but not soldered, to this bolt. The upper, or open, end of the resistance coil is found to pass from the outer surface of the cone through a groove to the inner surface, and down this to the bottom of the cone, where it is fastened to a rod which passes through the base and connects with the copper button at the bottom of the base. This wire running down the inner surface is now broken loose from its connection with the central bar. A loop should be bent in the wire, to prevent its slipping out of the slit in the cone and unwinding. It is the other electric terminal and may be connected to a No. 14 wire by means of a brass connector.



CROSS-SECTION OF ELECTRIC FURNACE

Place the element centrally within a common medium-sized flower pot; it must not touch the pot at any point. Pass the lower wire out through the hole in the bottom of the pot; the other wire can pass over the rim of the pot. Pack quicklime about the element, pressing down well, to within four or five cm. from the mouth of the cone. A ring of asbestos millboard may be cut to fit over the surface of the quicklime. Close the hole in the bottom of the pot with a cork. Set the whole thing on a brick, to protect the table. The two wires are now connected to a 110-volt supply. If it is desired to operate the furnace at a moderate temperature at first, any large resistance such as a rheostat, dilute solution of an electrolyte, or a similar heating element, should be connected in series with the furnace. It is not necessary to use these to protect the fuses; the furnace may be operated

directly on the line without danger, if 15-ampere or greater capacity fuses are used.

A small crucible can be placed in the interior of the cone, and brought to a temperature approaching 1300°C., or incipient white heat. This is sufficient for almost all analytic purposes. All the common fusion mixtures and fluxes can be melted into mobile liquids.

The furnace should not be operated for more than an hour at maximum temperature, as prolonged heating weakens the resistance wire and will ultimately cause it to part and arc; the core of the element will then usually crack, because of the intense localized heat. If a simple break occurs in the wire, without injury to the core, a new length of the wire (Nichrome or Chromel) may be purchased for a slight sum, and the core rewound with it.

A coating of alundum cement over the coils will make the device a permanent one, and will increase its maximum temperature.

Tube or combustion furnaces may be made similarly, using the now more common *cylindrical* heating elements.

Department of Agriculture Observing Goldenrod Rubber Experiments. The U. S. Department of Agriculture is watching the Edison-Ford goldenrod rubber experiments with interest, but is not carrying on any similar work of its own. The work is still in the non-commercial stage, and farmers are not being encouraged to figure on putting in a crop of goldenrod instead of corn or cotton next spring.

That Mr. Edison is really in earnest about finding some native plant that may serve as a source of home-grown rubber, at least in emergencies, is evidenced by the fact that he had a well-known New York botanist look over a vast number of plants. Over 1200 potential rubber bearers were examined and identified by this worker before Mr. Edison settled on the one species of goldenrod that is now engaging his attention.

Of the eighty or so distinct species in the goldenrod genus, only one has been selected as being the most promising of results in rubber. It is known to botanists as *Solidago leavenworthii*, and its range is restricted to a comparatively limited area in the southeast. It would probably grow well over a much larger territory, however, if it should prove profitable as a crop plant.

Mr. Edison has informed the Department of Agriculture that even within the limits of this one species there is a wide fluctuation in rubber content. One lot of plants may yield as little as one-half of one per cent on a dry weight basis, another as much as six per cent. The problem then becomes one of selecting the best strain and endeavoring to improve it by breeding.

If goldenrod cultivation becomes commercially profitable, its propagation will not offer any serious difficulties. Almost all of the species are perennials, sprouting freely from slender underground runners, and these rootstocks can be cut up in pieces to plant, like potatoes. Seed need not be used at all. In case a specially desirable strain of goldenrod should be developed, this vegetative propagation would be an advantage, for propagation by seed would permit such a hybrid to revert to its lower-grade ancestral condition, whereas planting by cuttings would keep it up to grade.—*Science Service*

A DEMONSTRATION OF CHANGES IN IONIC EQUILIBRIA DURING CHEMICAL REACTIONS

HOSMER W. STONE, UNIVERSITY OF CALIFORNIA AT LOS ANGELES, CALIFORNIA

Vivid, interesting experiments, presenting some of the fundamental concepts of the ionization theory for beginning students, are described in this paper. A striking demonstration is given of (1) the removal of ions by the formation of the weak electrolyte, water, in the reaction

$$H^+ + {}^-Cl + Na^+ + {}^-OH \longrightarrow H_2O + Na^+ + {}^-Cl,$$

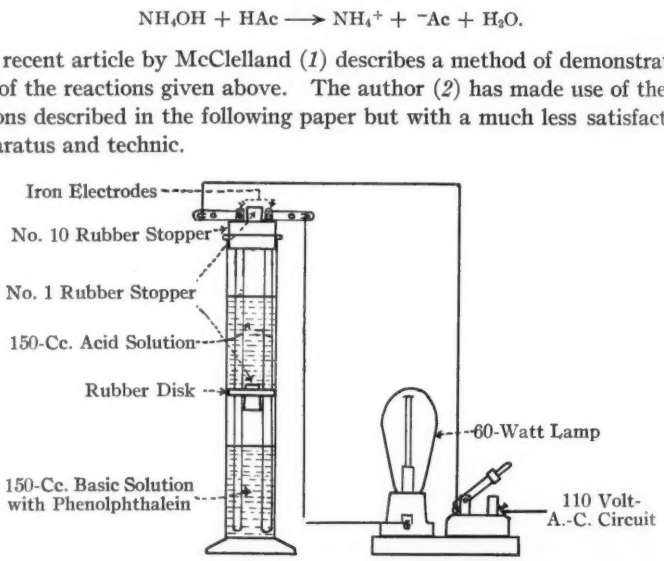
(2) the removal of ions by the formation of an insoluble precipitate in the reaction

$$Ba^{++} + 2{}^-OH + 2H^+ + {}^=SO_4 \longrightarrow BaSO_4 + 2H_2O,$$

(3) the formation of ions by the reaction of slightly ionized substances to form a highly ionized substance in the reaction

$$NH_4OH + HAc \longrightarrow NH_4^+ + {}^-Ac + H_2O.$$

A recent article by McClelland (*1*) describes a method of demonstrating one of the reactions given above. The author (*2*) has made use of the reactions described in the following paper but with a much less satisfactory apparatus and technic.



The accompanying drawing indicates the apparatus used in all three of these experiments. The electrodes are iron rods cut from ordinary ring stand supports. Any reaction between the iron rods and the acids is not noticeable since the solutions are dilute. The carbon rods formerly used gave trouble by breaking. The rubber disk at the center of the cylinder is a section cut from a No. 10 rubber stopper. The No. 10 stopper at the top of the cylinder and the rubber disk both have holes for the passage of the electrodes and a hole in the center which is closed by a No. 1 stopper.

The No. 1 stopper is inserted in the disk from below and in the No. 10 stopper from above.

The first experiment offers support for the assumption that the reaction between sodium hydroxide solution and hydrochloric acid solution reduces the total number of ions by half. This reaction as written in the first paragraph expresses that idea.

Tenth normal solutions of hydrochloric acid and sodium hydroxide are titrated, and then diluted to solutions of approximately 0.0006 *N* concentration, being made as nearly equivalent as possible by the usual quantitative procedure. The electrode assembly is removed from the cylinder and 150 cc. of the basic solution containing phenolphthalein are introduced from a pipet. The rubber disk is moistened with water to make it slide easily, and the electrode assembly inserted in the cylinder. The switch is now closed and the attention of the students directed to the intensity of the glow of the lamp. This glow is due to the conductivity of the sodium and hydroxide ions alone. The hydrochloric acid solution is now added and is supported by the rubber disk so that none gets down into the sodium hydroxide. The increased intensity of the glow of the lamp should be noted at this point. Now the solutions may be mixed by pushing out the stopper in the disk with a stirring rod, stoppering the opening in the No. 10 stopper, and inverting the cylinder and shaking. After the thorough mixing it will be seen that the lamp gives the same faint glow from the sodium and chlorine ions remaining that it did with the sodium and hydroxide ions in the original basic solution. The disappearance of the pink color of the phenolphthalein indicates the removal of hydroxide ions. Thus the experiment has furnished evidence for the theory that neutralization of such strong electrolytes is simply a reaction between hydrogen ions and hydroxide ions to produce undissociated water. Since these ions furnish half the conductance of the solution before mixing it is quite reasonable that the sodium and chloride ions remaining should conduct only as well as the original sodium and hydroxide ions in the basic solution alone.

The second experiment makes use of the same apparatus but substitutes 0.02 *N* barium hydroxide for the sodium hydroxide and 0.02 *N* sulfuric acid for the hydrochloric acid solution. In this case it should be noted that the light burns with almost full brilliance with the basic solution alone because of the greater concentration of the ions. On mixing, the disappearance of the pink of the phenolphthalein indicates the removal of the hydroxide ions as before. The formation of the cloudy precipitate of insoluble barium sulfate and the complete extinction of all glow from the light indicates the removal of the rest of the ions. Thus it is shown that ionic equilibria may be shifted toward completion by the formation of an insoluble electrolyte as well as by the formation of a slightly ionized substance.

The last experiment involves the use of 0.003 *N* ammonium hydroxide for the basic solution and 0.003 *N* acetic acid for the acid solution. With the basic solution in the cylinder alone or with both the basic solution and the acid solution in the separate compartments; the light should barely show any visible glow. After the solutions are mixed, the light should glow brilliantly. The application to the ionic theory can be made by pointing out that two weakly ionized electrolytes have reacted to form one strongly dissociated electrolyte and water.

The form in which the equations are written in the first paragraph is intended to emphasize the theory which the experiments are designed to demonstrate. Equations of this type which indicate the original reactants and the final products are spoken of as the equations for the main reactions by Bray and Latimer (*3*). In contrast with this form of equation, users of the ionic theory sometimes make use of equations designed to show the mechanism of the reaction. In such cases the ammonium hydroxide and the acetic acid would be shown as ionizing before any reaction could take place. However, there is nothing about this demonstration to indicate any such mechanism.

In conclusion the author wishes to acknowledge the kindness of G. Ross Robertson and Leon Robinson in making certain suggestions used in the experimental work described in this paper.

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(*2*) STONE and DUNN, "Experiments in General Chemistry," McGraw-Hill Book Co., Inc., New York City, **1929**, pp. 42–6.

(*3*) BRAY and LATIMER, "A Course in General Chemistry," Macmillan Co., New York City, **1926**, p. 6.

Persons Drinking Lemonade Made in Enamel Pails Get Antimony Poison. Ice-cold lemonade made in enameled pails bought especially for the purpose caused a severe though brief outbreak of illness among the 70 employees of a firm at Newcastle-upon-Tyne, England. The actual cause of the illness was antimony poisoning. The pails in which the drink was prepared were not made for cooking purposes and the cheap enamel glaze on the inside contained antimony oxide equivalent to 5 per cent of metallic antimony, which the acid of the drink dissolved. The drink was made from prepared "fruit crystals" which contained tartaric instead of citric acid, and after preparation was allowed to stand in the pails overnight, to be iced, sweetened, and served the next day. The drink had been prepared by the firm for the benefit of its employees during the extreme hot weather. The investigators comment on the unfortunate ending of this good intention and state that enamel containers intended for cooking, which the pails in question were not, are given a glaze which is so adjusted that the ordinary acid solutions used in cooking will only remove inappreciable amounts of antimony, and are thus safe to use.—*Science Service*

Correspondence

TRAINING IN WRITING CHEMICAL EQUATIONS

DEAR EDITOR:

How absurd it would be to deny a youngster the use of hammer, saw, square, or compass until he becomes mature enough to accept a contract for the construction of a modern dwelling.

I have been a subscriber and an interested reader of the JOURNAL OF CHEMICAL EDUCATION from its inception. I was among those who signed a paper promising a subscription before the magazine became a reality. It has developed to such an extent that now any one issue is worth the yearly subscription price.

In the last issue (September) I was particularly interested in Mr. Oser's article, "Training in Writing Chemical Equations."[1] With but one outstanding exception I think he has written a very valuable portrayal of the situation.

I, too, have heard many students say, to quote Mr. Oser, "I don't know what forms," "I don't know the formula," "I can't make it balance." But I don't hear such statements as often now as was the case a few years ago. This in spite of the fact that I am inclined to agree with Mr. Collier, Jr., when he said in his paper entitled "Methods of Increasing Interest in High-School Chemistry,"[2] presented before the Division of Chemical Education of the American Chemical Society at the Atlanta meeting, April 7–11, 1930—"The mental age of high-school students is growing lower every year."

Mr. Oser's discussion of the difficulties high-school students have in writing chemical equations was indeed very apt and to the point but he missed the best bet of all, not only did he overshoot, but ended his article by condemning it in no uncertain terms, *viz.*, "A New Tendency and a Poor One." To quote him further—"In order to make a good showing in standard tests, some teachers and some textbooks begin the teaching, if it can be called that, of chemical equations with the very first chemical change studied, or else at the very beginning of the chemistry course."

For several years I followed the procedure of waiting until what was supposed to be the logical time to present chemical equations. There always seemed to be a great deal of wasted energy and too many casualties. I felt there should be a better way out. So about five or six years ago I started easing the chemical equation idea, including definite knowledge of atoms, molecules, symbols, and formulas, into the student right from

[1] J. CHEM. EDUC., **7**, 2127–30 (Sept., 1930).

[2] *Ibid.*, **7**, 2141–9 (Sept., 1930).

the start and now I wouldn't for a moment consider going back to the old method.

I most certainly do not intend to imply that I am entitled to any credit for a new tendency and I am pleased to know there are other teachers who have tried it and therefore know its worth. I am positive it has little to do with the idea of making a good showing in standard tests, Mr. Oser notwithstanding, but rather to teach the young hopefuls the idea of chemical equations without inflicting too much torture. Perhaps some new tendencies are poor, even harmful, but this is one that should be given a fair trial by instructors who are experiencing difficulty with teaching students to understand and write chemical equations.

Yours very truly,

C. R. PETERSON

BILLINGS HIGH SCHOOL
BILLINGS, MONTANA

And Now Cheap Lithium. Lithium, the metal, is the lightest known solid. It is only a little more than half as heavy as water: light enough to float on ether or the lightest gasoline. Cork and balsa wood appear to be lighter than lithium because they contain pores filled with air.

The element lithium is very widely distributed, being found in traces in almost all minerals, but only in a very few is it present in amounts great enough to serve as ores.

The metal has most remarkable chemical activity of a type to make it useful as a "scavenger" in purifying metals. It is said to be able to remove carbon, sulfur, phosphorus, oxygen, nitrogen, and other impurities from alloys and pure metals. It is even claimed that if lithium is melted in an iron vessel, the latter becomes so porous by absorption of the foreign constituents by the lithium, that the lithium trickles through it. Also, that when lithium is melted in a glass or quartz vessel, the lithium reduces the silica to silicon, causing the container to crack.

A few hundredths of a per cent of lithium, added to aluminum or its alloys, is said to produce a degree of hardness not otherwise obtainable. Such an alloy is "Skleron." A small fraction of a per cent of lithium added to lead makes a suitable bearing metal. This is the "Bahnmetall" (railroad metal) extensively used on German railways.

The pure metal is very unstable in the air and causes water to decompose at ordinary temperatures. For shipment, the metal is best sealed into tin cans from which the air is removed.

When heated to just above its melting point, 365°F., lithium burns with a dazzling white flame. Its salts, however, color flames a brilliant cherry red. Lithium salts were long but erroneously supposed to be valuable in ridding the system of uric acid, and many thousands of dollars have been spent by rheumatic patients for "lithia waters," the curative powers of which were probably negligible. A fair-sized use for lithium salts is in the Edison storage battery, where a valuable service is performed in increasing the electrical capacity of the cells.

Almost simultaneously large-scale processes for the production of lithium have been developed recently in the United States and in Germany. A cost of $25 per pound in quantity has been mentioned and if this price can be bettered or even maintained in continued operation we may look for many new and interesting commercial applications.—*Ind. Bull., Arthur D. Little, Inc.*

Chemical Digest

ABSTRACTS

APPARATUS, LABORATORY PRACTICE, AND DEMONSTRATIONS

A New Apparatus for the Automatic Determination of Water by Distillation. J. PRITZKER AND R. JUNGKUNZ. *Chem.-Ztg.*, **53**, 603 (Aug. 3, 1929).—The apparatus which can be used with substances both lighter and heavier than water consists of the head piece (Figure 1) and the cooler (Figure 2). The tube *D* of the head piece is sealed to a

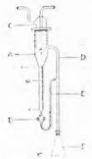


FIGURE 1

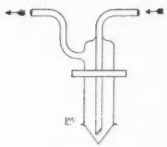


FIGURE 2

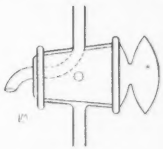


FIGURE 3

larger tube *A* which at its lower part is sealed to a graduated tube having a capacity of 15 cubic centimeters. A stopcock *B* (Figure 3) is located at the bottom of this graduated tube. A very narrow tube *E* leads from *B* back to *D*. At the lower end of the cooler which is drawn out to a point there are some glass projections which assure the central position of the cooler and prevent it from touching the inner walls of *A*. Any droplets collecting in the tip fall directly into the measuring tube. The places where the water enters and leaves the cooler are designated by arrows.

In order to avoid fires it is best to use halogenated hydrocarbons which in general are heavier than water. The substance to be analyzed usually floats on the surface of halogen compound. The most suitable substance was found to be acetylene tetrachloride which has a boiling point of 144°C.

FIGURE 4

The following method is used: Place 60 cc. of the halogen derivative and 10 to 20 grams of the substance to be analyzed in a 250-cc. Erlenmeyer flask *F* made from glass, copper, or iron. Attach the flask to the head piece by means of a cork stopper. Open *B* and let enough of the halogen compound flow into the graduated tube so that a little of it will pass into the tube *D*. Attach the cooler and heat until no more drops appear in *D*. The quantity of water collected can be measured directly on the graduated tube. In taking the reading it is best to note the upper and lower meniscus (Figure 4).

L. S.

The Preparation of Carbon from Marble. S. GENELIN. *Z. physik. chem. Unterricht*, **43**, 164 (July-Aug., 1930).—Fill a cup-shaped test glass about one-third full with dilute hydrochloric acid. Add a few pieces of marble. Fill an iron spoon with powdered magnesium, light the latter, and hold the burning magnesium above the surface of the liquid in the space of the vessel which has been filled with carbon dioxide gas. Keep it there until the flame of the burning magnesium has been extinguished and no more glow can be noticed in the spoon. The cake in the spoon will contain a large amount of shiny, black carbon.

L. S.

A Sensitive Method for the Determination of Refractive Indices. S. A. KORFF AND J. Q. STEWART. *Rev. Sci. Instruments*, **1**, 341–6 (June, 1930).—A combination of Michelson interferometer and spectroscope is described which has proved useful in giving accurate results of the refractive indices of vapors, especially near absorption lines. The method involves measurements, easily made, of wave-lengths of fringes seen in the spectroscope. Photographs of the fringes are given. The combination also provides an interesting method for putting along the spectrum a natural scale of frequencies, provided by these fringes.

R. L. H.

An Experimental X-Ray Tube. W. M. ROBERTS. *Rev. Sci. Instruments*, **1**, 473–8 (Aug., 1930).—A description is given of an X-ray tube which has the educational value

of being completely and easily dissectible. The student may take it apart and reassemble it in the various forms of gas or electron tubes. This feature also permits the study of various types of electrodes; of the influence exerted on discharge, in gas tubes, by the size and shape of the tubes, or by the position of the electrodes. Illustrations are included. R. L. H.

A Continuous Reading Aneroid Manometer for Moderately Low Pressures. E. A. STEWARDSON. *J. Sci. Instruments*, **7**, 217–21 (July, 1930).—A description is given of a manometer of the deflection membrane type, which is of very simple construction. It is sensitive to pressure differences of the order 10^{-4} mm. of mercury, and has been found in practice to be very constant and reliable. R. L. H.

The Determination of Minute Amounts of Iodine in Soils and Waters. R. L. ANDREW. *Analyst*, **55**, 269–77 (Apr., 1930).—A detailed discussion is given for the determination of minute amounts of iodine. The loss of iodine due to heating is accounted for. Tabulated results are also included. R. L. H.

Elementary Textile Microscopy. J. H. SKINKLE. *Am. Dyestuff Reporter*, **19**, Part I, 295–300 (May 12, 1930); 330–4 (May 26, 1930); Part II, 359–62 (June 9, 1930), 409–11 (June 23, 1930); Part III, 427–31 (July 7, 1930), 449–54 (July 21, 1930).—A discussion is given of textile microscopy which is intended for those who are not advanced in this type of work. In Part I the author describes fully types and uses of microscopes. Part II is a discussion of the methods of textile microscopy, and Part III has to do with identification by means of the microscope. R. L. H.

KEEPING UP WITH CHEMISTRY

Metals and Cosmetics at Ur. ANON. *Nature*, **126**, 182 (Aug. 2, 1930).—Dr. A. K. Graham of the Towne Scientific School of the University of Pennsylvania has made a chemical examination of some of the finds in the antiquities obtained from Ur. While the early bronzes are of a composition and quality that have never been surpassed, the silver and gold are not of a corresponding purity. The workmanship especially of the silver utensils is such as to command admiration. Some of the objects would be an achievement for a modern silversmith to produce. One silver bowl, for example, was first cut from a sheet of silver alloys cast in a convenient form. In hammering it into the finished shape at least three to five annealings would be required.

A chemical examination of the cosmetics used by Queen Schubad shows that both eyebrow and lip paint contained a large and dangerous quantity of lead. One sample of the light blue clay was probably powdered turquoise. A black powder similar to antimony on "Kohl" contains a large quantity of manganese and lead with a small quantity of copper, aluminum, phosphate, carbonate, silica, and iron. The latter probably came from turquoise. The black color was due to the black oxide of manganese. When mixed with oxides of lead various shades of brown, red, and purple could be obtained.

(The original paper of Dr. Graham was published in the *Museum's Journal*, Philadelphia, September–December, 1929.) F. B. D.

Spraying Quartz. EDIT. *Tech. Rev.*, **32**, 295 (Apr., 1930).—"Visitors who properly time their call at the Thomson Laboratory of the General Electric Company at Lynn, Mass., may observe the spectacular process of making mirrors of melted quartz sand and a shower of melted powdered silica glass (quartz). The powder, melted by a roaring oxygen-hydrogen torch at a temperature of 3000 degrees, is sprayed upon the quartz sand in order to obtain a mirror surface which may be ground to the delicate contours required for use in telescopes.

"The process, developed by Dr. Elihu Thomson, is to be used for making the gigantic 200-inch telescope mirror required by the great telescope that the California Institute of Technology plans to set up to supplement the work of the Mount Wilson Laboratory.

"If a mirror with the diameter of 200 inches were constructed of glass, the variations in its form induced by temperature would be so serious as to produce bad distortions in the image which it would give. Quartz remains practically constant under all ordinary temperatures. Consequently a mirror made of it would be easier to grind and to use upon completion."

A brief summary of Dr. Thomson's scientific achievements is appended. S. W. H.

Applying Aluminum in Petroleum Refinery. S. GILL. *Chem. & Met. Eng.*, **37**, 482 (Aug., 1930).—Due to the development of fields producing oils with high sulfur content the use of aluminum has increased in the petroleum refining industry. The possibility of obtaining aluminum or its alloy materials of light weight, great strength, and high resis-

tance to corrosion makes them applicable under a wide variety of conditions. R. L. H.

Phenol—A Survey of a Revived Industry. J. BEBIE. *Chem. & Met. Eng.*, **37**, 473–6 (Aug., 1930).—There are two types of methods for the manufacture of phenol: (1) recovery from certain fractions in the distillation of coal tar, (2) chemical processing of benzene. Before 1914 the American production of phenol was exclusively from coal tar, which amounted to about 1,000,000 lb. per year. Most of the domestic demand was supplied by imports from Europe. The war, which cut off imports, caused an increase in domestic production for explosives, and in 1918 1,000,000,000 lb. were produced. Most of the phenol is now produced by the synthetic process. This is due to the difficulty of separation and purification of phenol from tar. There are yet several possibilities whereby phenol may be derived from coal tar as a by-product. Synthetic phenol is derived by two processes: (1) by sulfonating benzene and fusing the sodium benzene sulfonate with caustic soda; (2) by chlorinating benzene and heating the chlorobenzene with caustic soda under pressure. R. L. H.

Adventures in Radiation. Finding New Uses for the Ultra-Violet. D. C. STOCKBARGER. *Tech. Rev.*, **32**, 185–8, 210 (Feb., 1930).—This article describes the work of the new radiation section of the Electrochemical Laboratory at the Massachusetts Institute of Technology.

"The problems presented for study are numerous and varied in character. They have to do with the manufacture of cloth, paper, rubber, leather, tin cans, glass, arc lamps, incandescent lamps, varnish, chemicals, fire alarm boxes, and photo-electric cells. They pertain to questions of health, safety, communication, television, and even magic.

"It may seem strange that the comparatively new laboratory should have so many contacts with industry, and that such mysterious looking experiments as are in progress should have commonplace, practical applications. This is so because this laboratory places particular emphasis on the study of ultra-violet radiation which has found a place of increasing importance in everyday life." S. W. H.

Increasing Solubility and "Binding Effects." EDIT. *Silicate P's & Q's*, **10**, 1–2 (Aug., 1930).—Application of binders and adhesives depends somewhat upon their solubilities. Applied to silicates, there are a number of ways of increasing such solubilities. One is to increase their alkalinity. If this method is used such silicates when used as binders of refractories have a lower melting point. By using water, the solvent in the vapor form solubility may be more readily attained. Another procedure that facilitates solution is: the solute is turned into such finely divided particles that they are almost microscopic in size. This is accomplished by the aid of an atomizer. This thoroughly pulverized solute before it is used is dried while still suspended in the air.

In addition to use in binding refractories silicates are also now used to cement the ingredients of dynamo brushes together. The silicate not only binds but resists the temperatures generated by sparking and the resistance which is ever present at their contacts. B. C. H.

The Use of Oxygen in the Manufacture of Producer Gas. A. E. R. WESTMAN. *Can. Chem. Met.*, **14**, 229–33 (Aug., 1930).—A comparison is made of the different methods of producing gas from coke, air, and water. The processes described are the air producer process, the oxygen producer process, and the water gas process. Tables are given including equations involved and heats of reactions. R. L. H.

The Uses of Nickel Brasses. S. B. SEELEY. *Metals and Alloys*, **1**, 657–9 (Aug., 1930).—There are at present a large variety of nickel brasses with a wide range of application. The paper is confined to alloys containing 60% copper, 5–30% nickel, and the remainder zinc. With 18% nickel the brass has a decided silver luster, with a slight increasing yellow tinge with 15% nickel. The yellow increases and at 5% nickel the alloy has the appearance of a very light colored brass—almost white. These alloys are mostly used for ornaments of various kinds. The percentage of nickel is given in each class of ornament. R. L. H.

The Development of Views Regarding the Nature of Chemical Forces. See this title on page 2730.

The Progress of Organic Chemistry. 1924–1928. See this title on page 2730.

Rhenium. See **German Chemical Society** in **Local Activities** on page 2749. O. R.

Starch. See **Alabama Polytechnic Institute** in **Local Activities** on page 2737. O. R.

SCIENTIFIC REVIEWS AND BIBLIOGRAPHIES

The Electronic Structure of Organic Compounds. I. W. D. HACKH. *Am. J. Pharm.*, **102**, 468–75 (August, 1930).—A description and explanation of the electronic structures of organic molecules and the polarity of these compounds, with illustrations

showing how the organic chemist uses the tetrahedron as the geometrical form of the carbon atom. The cubical atom of Lewis merges into the tetrahedral atom merely by drawing the electrons together so that the eight electrons situated at the corners of the cube become four electron pairs situated at the corners of the tetrahedron. A simpler explanation pictures the tetrahedral atom by four vectors running from the center to each of the four imaginary corners. G. O.

The Progress of Organic Chemistry. 1924–1928. III. ERICH LEHMANN. *Z. angew. Chem.*, **43**, 635–42 (July 12, 1930); 650–5 (July 19, 1930); 669–72 (July 26, 1930); 680–6 (Aug. 2, 1930); 708–11 (Aug. 9, 1930). Cf. J. CHEM. EDUC., **7**, 1197 (May, 1930); 1417 (June, 1930).

Continued from p. 627. 2. Aromatic Compounds: *a.* Monophenyl Compounds: General Discussion, Hydrocarbons, Substitutions, Oxy-Compounds (Phenols, Alcohols), Oxo-Compounds (Ketones, Aldehydes), Oxy-Oxo-Compounds (Oxy Aldehydes).

Continued from p. 642. a. Oxy-Oxo-Compounds (Oxy Ketones, Chinone Thio-Compounds), Acids and Their Derivatives, Nitrogenous Monophenyl Compounds.

Continued from p. 655. b. Polyphenyl Compounds: Diphenyl, Triphenyl, Polyphenyl Alkalene.

Continued from p. 672. c. Condensed Systems: α-Naphthalene and Acenaphthene Group: General Discussion, Oxy- and Oxo-Compounds, Acids, Dinaphthalene, Acenaphthene. β-Anthracene Group: General Discussion, Oxy- and Oxo-Compounds, Acids, Naphanthracene, Dianthracene.

Continued from p. 686. γ-Indene Group: Derivatives of Indene and Indane, Indanone, Diindene, Succindene. δ-Fluorene Group: Fluorene Derivatives, Difluorene, Fluoranthene. ϵ-Phenanthrene Group: Oxo Compounds. ζ-Higher Condensed Systems: Rubrene, Rubicene, Perylene. L. S.

Recent Advances in Science: Physics. L. F. BATES. *Sci. Progr.*, **25**, 6–11 (July, 1930).—A review of recent work on the following topics: the abundance of isotopes, the law of magnetization of solid crystals, supraconductors, and the measurement of dielectric constants. A. E. C.

Heat and Cold. A. B. NICHOLS. *Am. J. Pharm.*, **102**, 425–54 (August, 1930).—A rather extensive discussion of heat and its uses, its measurement, and place in our daily lives. Development of the thermometer and the making of thermometers are given with illustrations. Thermoelectric instruments, resistance thermometers, radiation thermometers, and low-temperature thermometers are some of the interesting instruments discussed. The thermometer is being investigated now as the "divining rod" to locate oil deposits and certain mineral deposits by relying on the suspected fact that the temperature rises in the vicinity of oil, coal, and salt deposits. G. O.

The High-School Science Library for 1929–1930. H. A. WEBB. *Peabody J. Educ.*, **8**, 35–48 (July, 1930).—This is the sixth library which Doctor Webb has spread before the science teachers in as many years. Those acquainted with his previous offerings will find this one conforming to the price-level arrangement of former lists. The list is also subdivided into: Introductions to Science, Science in the Home and Community, Clothing We Wear, Forms of Land and Water, Exploration and Travel, Flying and Fliers, How We Communicate, Worlds in Space, Living Creatures of Earth, Man as a Living Creature. This list contains 263 titles distributed under the above captions.

He states, "Certain fields of science are 'booming,' aviation, for example, and health. Publishers keep up with popular interest in their offerings. . .There is every reason why a high-school library, in its field and on its level, should keep abreast of current progress as indicated by books that are 'born' each year." B. C. H.

HISTORICAL AND BIOGRAPHICAL

Henri Le Chatelier. Reprinted from *The Metallographist* for October, 1901, by The Boston Testing Laboratories, Boston, Mass. This reprint contains a brief biographical note on Le Chatelier, a resumé of his researches, and a list of his publications dealing with metallographic and related subjects. M. W. G.

Cinquantenaire Scientifique de M. Henry Le Chatelier. This booklet was printed by Imprimerie F. Dutal, 21, Boulevard du Temple, Paris, **1922**, and contains an account of the celebration held in Professor Le Chatelier's honor in the chemistry amphitheater of the Sorbonne on January 22, 1922. M. W. G.

Dr. Georg Hevesy. See **Cornell University, Ithaca, N. Y.**, in **Local Activities** on page 2739. M. W. G.

The Development of Views Regarding the Nature of Chemical Forces. K. FAJANS. *Science*, **72**, 99–107 (Aug. 1, 1930).—Introductory public lecture of the non-resident lecturer in chemistry at Cornell University.

Historical—beginning with the 17th century but largely concerned with modern views of molecule and crystal structure. Diagrams and references. G. H. W.

The **Seventieth Birthday of A. v. Weinberg.** P. WALDEN. *Z. angew. Chem.*, **43**, 706–8 (Aug. 9, 1930).—Dr. A. v. Weinberg is not only a dye chemist and an inventor but an independent, highly scientific thinker. This is evident from his articles on the kinetic stereochemistry of carbon compounds, chemical action between molecules, atomic valences, energy relationships (heat of combustion and dissociation), structure of benzene, the assumption of rotating and vibrating atomic movements within the molecule, the formation of chemical elements, and the chemistry of the stars. L. S.

The **Seventieth Birthday of A. v. Weinberg on August 11, 1930.** L. GANS. *Z. angew. Chem.*, **43**, 703–6 (Aug. 9, 1930).—At the age of 23 A. v. Weinberg became a chemist at the Casella Dye Works in 1883 after having studied with Fittig at Strassburg and having received his doctor's degree under Baeyer in Münich. Two years later he took out his first patent on the preparation of Naphthol Black, a bluish black diazo dye. During the forty years of his connection with this plant he rose from the position of a routine laboratory chemist to that of one of the heads of the company. The *Berichte der Deutschen Chemischen Gesellschaft* contain a large number of his articles on coal-tar dyes. He is one of the founders of the University of Frankfurt a. M. He is a leader of chemical thought in Germany. L. S.

The Seventieth Birthday of Dr. Arthur v. Weinberg. R. LOEWENTHAL. *Chem.-Ztg.*, **54**, 617 (Aug. 19, 1930).—Dr. Arthur v. Weinberg celebrated his seventieth birthday on August 11th. He distinguished himself by his outstanding work on coal-tar dyes in the aniline dye works of Leopold Cassela and Co., a company which had been founded by his father and Dr. Leo Gans. He invented a large number of important dyes that are used even today. At the end of the last century he became one of the directors of this company until it was taken over by the I. G. Farbenindustrie. He had received several honorary degrees. L. S.

The Seventieth Birthday of Dr. Carl Paal. M. BUSCH. *Z. angew. Chem.*, **43**, 631–2 (July 12, 1930).—Dr. Carl Paal celebrated his seventieth birthday on July 1st. He was born in Salzburg as the son of a lawyer and grew up in the house of his grandparents. He studied chemistry at the Universities of Münich and Berlin. In 1883 he published his first article on the action of acetyl chloride on benzaldehyde. In 1884 he went to Emil Fisher in Erlangen where he received his degree with high honors. In 1890 he started his teaching career at Erlangen, rose rapidly in rank, and in 1912 he became the successor of Ernst Beckmann as Director of the Laboratory for Applied Chemistry and Pharmacy at Leipzig.

Dr. Paal has done a large amount of research work in various fields of chemistry. He worked on ketones and derivatives of thiophene, synthesized pyridines and piperidines, heterocyclic bodies and unsaturated amines of the aliphatic series, amino sulfonic acids, and colloidal solutions of metals of high concentrations and stability. He studied the riddle of the protein molecule, hydrogenation of unsaturated compounds, and analytical determinations and analyses of foods.

He has been honored publicly several times and is beloved by his students and coworkers. L. S.

Metals and Cosmetics at Ur. See this title on p. 2728.

Dr. Elihu Thomson. See **Spraying Quartz** on p. 2728.

American Chemical Society. Twenty-five Year Summary, Growth, and Business Management. See this title, p. 2733.

EDUCATIONAL MEASUREMENTS AND DATA

Rehabilitation in Arithmetic with College Freshmen. T. E. CARLSEN AND L. R. WHEELER. *Peabody J. Educ.*, **8**, 24–7 (July, 1930).—Many teachers' colleges are requiring that their freshmen meet eighth grade standards in arithmetic. This study as well as one made at Miami University finds that approximately forty-two per cent of their freshmen are below the eighth grade standard.

An analysis of student errors in the study grouped them as: 1, combinations; 2, common fractions, especially division; 3, decimal fractions; and 4, denominate numbers. Lessons were given a group of those who were below standard and their improvement tested until they attained the desired rating. In four weeks sixty-five per cent of the delinquents were brought up to the eighth grade standard and in eight weeks ninety-five per cent were thus reclaimed. B. C. H.

The Relation of Intelligence to Student Teaching Success. F. L. WHITNEY AND C. M. FRAZIER. *Peabody J. Educ.*, **8**, 3–6 (July, 1930).—After a brief compilation of

previous studies of the above relation the authors report an investigation of their own which used a select group of teachers in training. With this group, another as a "control," and of almost equal size of a more heterogeneous character was studied.

The homogeneous group was chosen so that all were women with no teaching experience. They had all entered college immediately following graduation from high school and were between the ages of twenty and twenty-five. They all did their practice teaching in either the fourth, fifth, or sixth grades.

Some of the summary conclusions from all studies made upon this general problem are:

1. There is little relationship between intelligence as measured by current tests and student teaching success.
2. There is a significant relationship between academic success and intelligence test ratings.
3. Intelligence tests now in use are not good measures of teaching intelligence, no matter how well they measure abstract intelligence. B. C. H.

THE PHILOSOPHY OF EDUCATION

Scholars and Schoolmasters. EDIT. *Harvard Alumni Bull.*, **32,** 597 (Feb. 20, 1930).—"Scholarship threatens to ruin education. This is the opinion of Professor David Snedden of the Teachers' College, Columbia University, as expressed in an article called 'The Hurtful Influence of Scholars on Useful Educations," in *School and Society*, for February, **1930.**

"The wording of the title is an indication of the temper of the article, which is that of a man who wishes to brush aside conventions for the vigorous presentation of realities. The argument may be summarized as follows: highly specialized scholarship has attracted an increasing number of able men and they wield a large influence in the making of school and college curricula. Their natural tendency is to insist on the value of the subjects they teach. They exert a strong influence to have these subjects taught in school and colleges as wholes, in logical organization, and for their own sakes. They view their subjects as ends, not means, they want boys and girls to know these subjects fully, to pursue them from their very foundations, as if the object in view were scholarship itself, and to avoid any selection of special parts and phases of a subject on the ground of their connection with a job, or with citizenship, or with any interest in life.

"Schoolmasters, on the other hand, know that scholarship is not an end in itself. Dr. Snedden groups as 'scholars' all specialists, even athletic coaches; and in contrast he groups all curriculum makers as 'schoolmaster,' including deans, superintendents, college presidents and other like officers. The schoolmaster wants to break up subjects, use parts of a subject for one purpose and other parts for another purpose, combine parts of different subjects, and generally abandon logical order for psychological order. When a subject is used as a means of education, rather than an end in itself, its integrity as a subject cannot be sacredly maintained.

"There is weight to this argument, but there are grave dangers in accepting it, without criticism, as a guide for education. The aims of education must be stated in terms of the effect of studies and school activities and influences on the student; the whole end in view is the making of a man. In its intellectual aspects, and especially in what may be called the moral aspects of intellectual effort, education cannot ignore the fact that scholarly ideals contain in them something of value. If the student never studies any subject as a whole, in logical order, for the sake of knowing it as fully as possible on a given level, including its relations to other subjects and to his own various interests, he has missed a profitable intellectual experience.

"It is true that university specialists ought not to dominate the making of school and college curricula. It is also true that educational requirements, stated in terms of the study of specified groups of subjects, obstruct educational progress. And it is true that a curriculum which includes only scraps of subjects is not a good curriculum."
[Cf. Edit., J. CHEM. EDUC., **7,** 978–9 (May, 1930).] S. W. H.

CONTEMPORARY NEWS AND COMMENTS IN CHEMISTRY AND EDUCATION

A Demonstration of Confidence in Research. R. S. MCBRIDE. *Chem. & Met. Eng.*, **37,** 352–3 (June, 1930).—Confidence in the necessity of fundamental research is demonstrated by the Aluminum Company of America in its new million-dollar laboratory at New Kensington, Pa. A description is given of the building and laboratories with illustrations. R. L. H.

The **Seventieth Birthday of Dr. A. v. Weinberg.** See this title on page 2731.

The **Seventieth Birthday of A. v. Weinberg on August 11, 1930.** See this title on page 2731.

The **Seventieth Birthday of Dr. Carl Paal.** See this title on page 2731.

American Chemical Society. Twenty-five Year Summary, Growth, and Business Management. C. L. PARSONS. *Ind. Eng. Chem., News Ed.*, **8**, 1–3 (July 20, 1930). O. R.

Program of the Cincinnati Meeting of the American Chemical Society. ANON. *Ind. Eng. Chem., News Ed.*, **8**, 1–10 (Aug. 20, 1930). O. R.

Teachers to Commute by Air for Extension Courses. See **New York University** in **Local Activities** on p. 2741. O. R.

Dr. George Hevesy, George Fisher Baker Non-Resident Lecturer in Chemistry at Cornell University. See **Cornell University, Ithaca, N. Y.**, in **Local Activities** on page 2739. M. W. G.

Weights and Measures Library Presented to Columbia University. See **Columbia University, New York, N. Y.**, in **Local Activities** on page 2739. M. W. G.

American Association for the Advancement of Science. See this title in **Local Activities** on page 2735. M. W. G.

American Electrochemical Society. See this title in **Local Activities** on page 2735. M. W. G.

International Union of Pure and Applied Chemistry. See this title in **Local Activities** on page 2748. M. W. G.

League of Nations Committee on Intellectual Coöperation. See this title in **Local Activities** on page 2748. M. W. G.

FOREIGN CHEMICAL AND EDUCATIONAL CONDITIONS

Report on Indian Education. See **U. S. Office of Indian Affairs** in **Local Activities** on page 2736. M. W. G.

The Public Library System of France. See this title in **Local Activities** on page 2749. M. W. G.

GENERAL

Can Americans Be Scientists? Our Contributions to Physical Science. J. MAYER. *Tech. Rev.*, **32**, 254–6 (Mar., 1930).—"We are a great business people, but superficial, materialistic, and quite untouched by considerations of scholarly tradition; such is the usual estimate of the United States vouchsafed by Europeans and generally accepted by Americans, sometimes with pride. To most of the outside world and to some of us, the United States is the nation of the almighty dollar and little else. When Edison and the Wright brothers are named and a share of the development of science is claimed through them, the critics hasten to concur, only to adduce this as proof strengthening their assertion, since these men have applied the results of scientific achievement to the practical arts only, and have seemingly left us as far as before from the plane of Galileo and Newton.

"And yet this estimate is entirely false, for instead of being but negligible laggards after science, America today definitely leads the vanguard with three other nations, Germany, England, and France. We have produced at least ten times as many great scientists in the last century as has, for instance, Italy, the home of Galileo."

The above is the introduction to a description of the scientific achievements of Benjamin Franklin (1706–1790), Count Rumford (1753–1814), John Winthrop and David Rittenhouse of the eighteenth century; and Joseph Henry (1797–1878), Josiah Willard Gibbs (1839–1903), H. A. Rowland (1848–1901), Michelson and Morley, and Theodore William Richards in the 19th century.

America's contributions during the first quarter of the twentieth century far outrank those of any other nation. Rutherford (1846–1892), Pickering (1846–1819), Abbé (1838–1916), Newcomb (1835–1909), and Hill (1838–1914), all are names marking definite mileposts in the science of astronomy.

"Leaders of industry and public affairs alike realize that manufacturers and capitalists of America today, whose immense fortunes are built upon the findings of the man in the laboratory, are awake to their need of the service of the man of science, and the laboratory with its personnel has begun to appear as an integral part of the plans and the programs of an increasing number of business corporations. Laboratories in universities and other centers of research are commanding a recognition and giving an opportunity that at once indicates the necessity and insures the acceptance of research in all fields of science."

The article is illustrated. S. W. H.

The Sick Textile Industry. H. S. BUSBY. *Tech. Rev.*, **32**, 288–90, 318 (Apr., 1930).—"During the latter days of the eighteenth century, the manufacture of cotton fabrics was revolutionized by the great English inventors. Inventing ingenious machinery for which Eli Whitney was to gin cotton and Watt to furnish power, Wyatt, Highs, Hargreaves, Arkwright, and their contemporaries ushered in the machine age. In volume, the output of the textile industry forthwith grew enormously, and the example set of large-scale machine production spread quickly to other types of manufacturing.

"Hereupon arose a paradox. The industry that ushered in our modern machine era did not keep pace in technical improvements or managerial technic with the other industries which imitated its methods. The American textile industry today, except in size, is not greatly different from the textile industry that that young expatriate Englishman, Samuel Slater, found in Rhode Island in 1790.

"The textile industry needs scientists and engineers. It needs laboratories. It is sick because its diet has included but a limited amount of the vitamins of pure science. It is sick, too, because it never has been willing to submit to managerial therapy of the kind that good sound economists have developed. The textile industry has hardly discovered scientific management. It is high time that our technical schools supply to the industry men who can bring to it these things. It must get in step with modern business, accept readjustment of wages and hours as right and proper, prohibit overproduction, eliminate the waste chargeable to small units, and control its own marketing system." Illustrated. S. W. H.

"Nothing New under the Sun." EDIT. *Am. J. of Pharm.*, **102**, 423–4 (Aug., 1930).—A hackneyed phrase but a clever editorial revealing that so-called modern devices are nothing but "ancient performances ensembled in up-to-date trappings." G. O.

Reminiscences of an Expert. H. LEFFMANN. *Am. J. Pharm.*, **102**, 455–67 (Aug., 1930).—An article containing first-hand information on the methods of expert testimony of chemical analyses. G. O.

Sub-Atomic Energy. EDIT. *School*, **41**, 828 (July 17, 1930).—Sir Arthur Eddington is quoted as saying, "There is enough energy in a drop of water to furnish 200 horsepower for a year." A 100,000 kilowatt generating station has to be surrounded by wharves and siding to furnish the fuel as a source of the power. If water's sub-atomic energy could be made available, a teacup of it, thirty grams, would supply the year's need.

"It seems quite plain that in the stars the 'cup of water' method of maintenance is actually in operation or at least there is some partial adaptation of it." To get this sub-atomic energy freed it is necessary to heat matter up to a temperature of thirty or forty million degrees Centigrade. There seems to be a temperature in that region at which matter yields its sub-atomic energy much as water boils at 100 degrees Centigrade. B. C. H.

How the Chemical Product Differs Economically. L. W. BASS. *Chem. & Met. Eng.*, **37**, 409–11 (July, 1930).—An unusually low ratio of wages to value added to raw materials by manufacture is characteristic of chemical industry in general. Statistical tables and discussion. O. R.

Research Scholarships and Fellowships Supported by Industry. C. J. WEST AND C. HULL. *Ind. Eng. Chem., News Ed.*, **8**, 3–6 (Aug. 10, 1930).—Addendum to previously published lists, to which reference is made. O. R.

Hydrated Lime Found Remedy for Serious Cabbage Disease. Clubroot of cabbage, one of the most serious of truck crop diseases, has met its Waterloo in hydrated lime, one of the commonest and cheapest of chemicals. H. L. Wellman of the U. S. Department of Agriculture, who has been working on the clubroot problem for several years in the great cabbage-raising area of Wisconsin, found that other forms of lime were ineffective but that hydrated lime, applied two tons to the acre, kept down the disease. Clubroot of cabbage is caused by a primitive organism called *Plasmodiophora brassicae*, which belongs to the class known as slime-molds, a group so far down on the evolutionary scale that it is not certain whether the creatures are plants or animals.—*Science Service*

Local Activities

Purpose and Organization

The purpose of the Local Activities Section of the JOURNAL OF CHEMICAL EDUCATION is briefly but clearly stated in its title. Any items of local news from educational or scientific institutions, A. C. S. Sections, Teachers' Associations, or other organizations which are of such a nature as to make them of more than purely local interest rightfully belong to this Section.

The responsibility of reporting items for this section rests entirely with the local institutions and organizations. It is desirable to have a representative appointed to report news regularly. Suitable material sent to the editorial office before the 20th of each month will be published in the following month's journal. The Editorial Staff must necessarily reserve the right to abridge or totally reject any items submitted. If the following suggestions are followed, however, the necessity for such action will be largely obviated.

Material to Be Reported

1. Notices of local scholarships or fellowships and announcements of new or unusual courses in chemical education or special fields of chemistry.
2. Reports of dedication of new science buildings, stressing the unique features.
3. News notes concerning activities of prominent scientists and educators and of the honors and awards made to them.
4. Promotions within, or changes of personnel of, a department.
5. Notices of any special gifts to chemical organizations or departments—as fellowships, endowments, laboratory gifts, library gifts, etc.
6. Accounts of meetings, social functions, exhibitions, chemical entertainments, etc., which might be suggestive to other organizations. Where original or unusual features are included, it is desirable that they be described in some detail.

GENERAL

American Association for the Advancement of Science. The fourteenth annual meeting of the Pacific Division of this association was held at the University of Oregon, Eugene, Oregon, from June 18 to 21, 1930, according to a report in *Science*. DR. O. F. STAFFORD, of the University of Oregon, a member of the staff of contributing editors of the JOURNAL OF CHEMICAL EDUCATION, was reëlected to the executive committee of the Pacific Division.

In conjunction with this meeting the third Pacific intersectional meeting of the American Chemical Society was also held. The participating sections were California, Northwest Utah, Oregon, Puget Sound, Sacramento, Southern California, and Washington-Idaho Border. The following papers were read at the general session: "Isotopes and Band Spectra," by R. P. BIRGE of the University of California; "The Application of X-Ray to Chemical Problems," by MAURICE L. HUGGINS of Stanford University; and "The Concepts of Physical Chemistry in Investigations of Vital Processes," by L. B. BECKING of the Hopkins Marine Station, Pacific Grove, California.

American Electrochemical Society. Science announces the fifty-eighth meeting of the American Electrochemical Society in Detroit, Michigan, September 25–27, 1930. Among the technical sessions was an informal round table discussion on electric furnace gray iron led by DR. RICHARD MOLDENKE. Visits were made to the plants of the Ford Motor Company, Parke, Davis & Company, Champion Porcelain Company, Hoskins Manufacturing Company, Ternstedt Manufacturing Company, and the General Motors Research Laboratories. By special invitation from MR. HENRY FORD, a trip was made to the Ford Village with its unique collection of old machinery and equipment of historical interest.

The Guggenheim Foundation. We learn from *Science* that DR. FRANK AYDELOTTE, president of Swarthmore College, and EYLER SIMPSON, both representatives of the Guggenheim Foundation, recently returned from an eleven weeks' tour of South America. Dr. Aydelotte and Mr. Simpson went to establish Guggenheim Scholarships in Argentina and Chile. The scholarships will allow $2500 yearly and traveling expenses.

Mining and Metallurgical Advisory Boards, Carnegie Institute of Technology and United States Bureau of Mines, Pittsburgh, Pennsylvania. At the fourth annual meeting on October 17th of the Metallurgical Advisory Board to the U. S. Bureau of Mines and the Carnegie Institute of Technology, a number of subjects of vital interest to the iron and steel industry were presented. New methods of refining steel, new conceptions of the function of slags in steel making, and new methods of determining various harmful impurities in steel were the topics of discussion.

The meeting opened in the auditorium of the Bureau of Mines with an address by DR. F. N. SPELLER, chairman of the advisory board and director, department of metallurgy and research, National Tube Company. Following this, metallurgists of the Bureau of Metallurgical Research, Carnegie Institute of Technology, gave a progress report on iron-manganese-carbon alloys. DR. F. M. WALTERS, JR., director of the bureau, DR. N. N. KRIVOBOK, DR. J. D. FRIAUF, MR. CYRIL WELLS, and MR. MAXWELL GENSAMER, associates, presented papers on different phases of this study.

During the afternoon session DR. C. H. HERTY, JR., physical chemist of the U. S. Bureau of Mines, and DR. G. R. FITTERER, associate metallurgist, presented an illustrated report on slag viscosity and deöxidation with aluminum-silicon alloys, and a progress report on fundamental studies in the laboratory. Dr. Herty reported on plant research in open-hearth steel.

U. S. Office of Indian Affairs. We quote from *School and Society* the following extracts from the report of CHARLES J. RHOADS, U. S. Commissioner of Indian Affairs:

"The program of Indian education and the courses of study offered in our Indian schools are being modified and expanded so as to place increasingly greater emphasis on education of a practical and vocational character so that upon completion of the prescribed courses the Indian boy or girl may be fitted to take his or her place in the life of the nation, whether as an industrial worker, an agriculturist, a teacher, clerk, or in some other of the innumerable ways in which American citizens earn their living.

"To assist in the reorganization of the Indian school service there has been appointed an assistant director of education, who was at one time dean of women at the University of Montana, and from 1921 to 1927 was associated with the employment service of the Department of Labor.

"A position of supervisor of trade and industrial training has been established, the appointee being a man who is peculiarly fitted for the development of the trade and industrial courses in the Indian schools. An examination has been announced by the Civil-Service Commission for the position of director of education in the Indian service to fill the vacancy caused by the transfer of the former director to the superintendency at the Haskell Institute, Lawrence, Kansas. Haskell is one of the best known and one of the largest Indian schools, and under his direction and in line with the new policy of Indian education we hope to develop it into a full junior college in which special vocational training will be given with a view of training students for real leadership among their people.

"A supervisor of elementary education has been appointed, and also a number of demonstration teachers to visit the schools, observe conditions, and suggest improvements in teaching and procedure. Increased emphasis is also being placed on home economics instruction for Indian girls.

"We propose to give the Indian a practical education, along vocational lines whenever possible, to make better provisions for his medical needs, to provide for the indigent, to assist him in finding and keeping a job, to increase the productivity of his land, and to give him the advantages of modern organization and

business methods to the end that we may hasten the day when he will be able to assume entire responsibility for caring for himself and his problems just as does his white neighbor. While this may involve for the time being an expansion of our activities, with increased appropriations and additional personnel, in the end it will prove true economy."

Yale Chemical Association. On September 27th, at a picnic and luncheon at Bethwood, the country estate of PROFESSOR TREAT B. JOHNSON of Yale University, the Yale Chemical Association was organized. Some sixty were in attendance. The officers of the new organization are: *president*, C. O. JOHNS, Standard Oil Development Co., New York City; *vice president*, E. B. HURLBURT, The J. B. Williams Co., Glastonbury, Conn.; *secretary-treasurer*, J. J. DONLEAVY, Yale University, New Haven, Conn.

The guest of honor was PROFESSOR EMERITUS WILLIAM G. MIXTER, for many years a member of the faculty of the Sheffield Scientific School. Several informal talks were made but the major part of the time was spent in the meetings between old friends and reminiscences of former days at Yale. The officers plan to reach all former students of Yale who are interested in chemistry, with a view to forming a strong and active association.

EDUCATIONAL INSTITUTIONS

Alabama Polytechnic Institute, Auburn, Ala. *Science* announces that the Alabama Polytechnic Institute and the Bureau of Standards are about to begin a coöperative research on starch at the newly opened chemical laboratories of the Institute at Auburn, Alabama. The investigation will have to do primarily with the starches found in crops in the South. A study will be made of the uses of starch in the manufacture of textiles, and the properties required in starch for each use. Further, it is planned to determine whether starch from one source is superior to that from another for a given purpose, and if specific starches may be modified so as better to adapt them for particular uses.

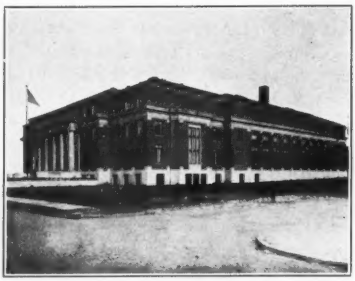
PRESIDENT BRADFORD KNAPP has announced that by special arrangement DR. CHARLES H. HERTY, the widely known industrial consultant, has been obtained as a special lecturer on chemical problems of the South and as a consultant on development of the department of chemistry and the chemical research work of the Institute. Dr. Herty will visit Auburn monthly to lecture to the students in chemistry and engineering, to consult with the president and faculty in chemistry regarding the work of the institution and to investigate the progress of the research work being conducted in chemistry and chemical engineering.

The American University, Washington, D. C. A new and modernly equipped laboratory for analytical and physical chemistry has been installed this summer and is now in operation. The laboratory desks are of steel with alberene tops and are capable of adequately accommodating sixteen students. Each desk contains taps for gas, water, air, steam, and electricity. The sinks are wide and spacious, easily accessible. Three open-type hoods have also been installed, two in the new laboratory and the third in the general chemistry laboratory. An electric distillation apparatus for distilled water, a new balance room with several new balances, and a hot plate complete the new equipment.

Marked increases in the registration for chemistry courses have necessitated this expansion of the department. The personnel of the department consists of ASSOCIATE PROFESSOR WILLIAM B. HOLTON (B.S., M.S., Ph.D., Illinois), head of the department and professor of general and organic chemistry, and DR. EDWARD WM. ENGEL (B.S., Union, A.M., Ph.D., Princeton), instructor of analytical and physical chemistry.

Battelle Memorial Institute, Columbus, Ohio. DR. HAROLD E. SIMPSON has been appointed a member of the Battelle Memorial Institute staff. He received both his undergraduate and graduate training at Ohio State University, where he specialized in ceramics.

Dr. Simpson has had considerable experience in industrial work dealing with



ceramics. He comes to the Institute from Rutgers University, where he held the position of assistant professor of ceramics.

Dr. Simpson will work under the direction of CLYDE E. WILLIAMS, assistant director, and R. A. SHERMAN, chief fuel engineer at the Institute, on a project dealing with the slagging action of coal ash on boiler furnace refractories. This is a study in coöperation with the American Society of Mechanical Engineers.

Boston College, Chestnut Hill, Mass. Boston College is offering in its extension school during the winter session a wide range of undergraduate courses, as well as advanced courses, leading to the M.S. degree in physical and advanced organic chemistry, organic analysis, chemical kinetics, electrochemistry, and atomic structure.

Bryan Memorial University, Dayton, Tennessee. *Science* announces that A. P. BJERREGAARD, until recently chief chemist for the Empire Refineries Division of Cities Service Company and lately doing consulting work, has been appointed professor of chemistry and dean of the science department in Bryan Memorial University.

Carnegie Institute of Technology, Pittsburgh, Penna. Evening courses of graduate grade are being conducted at the Carnegie Institute of Technology in advanced physical chemistry, theory and thermodynamics of solutions, and physical chemistry of metals. These courses are also open to undergraduates who can meet the prerequisites.

Centenary College of Louisiana, Shreveport, La. MR. FRED J. MECHLIN, chief chemist for the Louisiana Oil Company of Shreveport for the past several years and formerly an instructor in chemistry at Kansas University, has been appointed as associate professor of chemistry at Centenary College. MR. ROBERT FRYE, who has been associate professor of chemistry in the college for the past four years, has accepted a position as chemist with the Louisiana Pine Tar Products Company of Alexandria, Louisiana.

College of the City of New York. PROFESSOR RESTON STEVENSON has been elected secretary of the New York Section of the American Electrochemical Society for the year 1930–31.

PROFESSOR BENJAMIN HARROW attended the Second International Congress of Sex Research held in London, August 2nd to 9th, and read a paper on hormones.

PROFESSOR LOUIS J. CURTMAN published with S. EDMONDS, "The Separation and Detection of Oxalates in the Presence of Other Reducing Agents," in the June 20th issue of *Chemical News*. With S. LEIKIND, he also published "Transposition of Silver Bromide by NaCl Solution," in the May 30th issue of the same publication.

The following new members have been added to the staff of the department of chemistry: PROFESSOR ROSS A. BAKER, formerly of Syracuse University, now at the 23rd Street Center of City College;

MR. FREDERIC L. WEBER, formerly of the Brooklyn Center of City College, now transferred to the 23rd Street Center; MR. H. ROBERT CURTMAN; MR. CHESTER KREMER; MR. MARTIN PAUL; MR. MORRIS U. COHEN.

PROFESSOR HERBERT R. MOODY, director of the department of chemistry, has just returned to this country after an absence of seven months. He was on a term's sabbatical leave and toured Africa and Europe. In France and Italy he visited many of the large factories and universities. He also attended the convention of the Society of Chemical Industry in Birmingham, England.

Columbia University, New York, N. Y. *Science Service* announces that a weights and measures library of about 1200 volumes and 700 pamphlets and containing works from 1520 to the present time has been given Columbia University by SAMUEL S. DALE, of Boston, former editor of the *Textile World Record* and an authority on weights and measures.

Nineteen languages are found in the collection, which is the result of Mr. Dale's interest in the controversy over the proposed adoption of the metric system in the United States. It represents the accumulation of thirty years' research in this country and abroad to bring together, the donor announced, "as far as possible a copy of every book, pamphlet, government document, and other printed or written matter dealing with the origin, history, development, and science of weights and measures that has ever been issued in any language at any time."

DR. MARSTON TAYLOR BOGERT, it is reported in *Chemistry and Industry*, was recently elected to honorary membership in the Council of the Société Industrielle de Chimie. Among other foreign connections, Dr. Bogert is also an honorary member of the Chemical Society of Poland and of the Royal Bohemian Academy of Arts and Sciences and is the senior American past president of the Society of Chemical Industry.

Cornell College, Mount Vernon, Ia. DR. HAROLD L. MAXWELL, who for some years was a professor of chemistry at Purdue University, has gone to Wilmington, Del., as research chemist for the du Ponts. DR. GARRETT W. THIESSEN is the newly appointed professor of physical and analytical chemistry at Monmouth College, Illinois. J. B. SHUMAKER recently received the Ph.D. degree in food chemistry at the Iowa State College. ROBERT W. GETCHELL, professor of chemistry at the Iowa State Teachers' College, Cedar Falls, has recently received the Ph.D. degree at the University of Wisconsin. RALPH TALLMAN, who recently received the Ph.D. degree in chemistry at Cornell University, continues as assistant professor at Cornell.

All of the foregoing were chemistry majors and assistants in chemistry at Cornell College.

Cornell University, Ithaca, N. Y. The George Fisher Baker Non-Resident Lecturer in Chemistry for the present term is DR. GEORG HEVESY, professor of physical chemistry in the University of Freiburg, Germany. Professor Hevesy is a Hungarian by birth, having been born in Budapest in 1885. He first attended the University of Budapest, then the Technische Hochschule of Berlin, and later the University of Freiburg, where he received the degree of Doctor of Philosophy in 1908. After two years as assistant in the Technische Hochschule of Zürich, he carried on advanced research at Karlsruhe in PROFESSOR HABER'S Laboratory in 1910, and from 1911 to 1914 he held a research fellowship in the University of Manchester, working in the laboratory of SIR ERNEST RUTHERFORD. During this period he also carried on research work at the University of Liverpool in the laboratory of PROFESSOR DONNAN.

He was then called to a position in the Radium Institute of Vienna, and in 1920 he became a member of BOHR'S Institute of Theoretical Physics at Copenhagen. In 1926 he was called to the professorship

of physical chemistry at the University of Freiburg. While connected with Bohr's Institute he carried out, in coöperation with DR. COSTER of Holland, a brilliant

research that led to the discovery of the new element hafnium.

His many and diverse investigations have laid in the fields of inorganic and physical chemistry, electrochemistry, radioactivity, and the separation of isotopes.

During the coming term Dr. Hevesy will lecture on the following topics: "Chemical Analysis by X-Rays and Its Applications"; "Rare Earth Elements and Atomic Structure"; "Chemistry of Hafnium"; "Electrolytical Conduction and Diffusion in Solids"; "Separation of Isotopes."

The Institute of Paper Chemistry, Appleton, Wis. The new Institute of Paper Chemistry, located at Appleton, Wisconsin, and affiliated with Lawrence College, opened its first fall term on September 17th with a registration of fifteen graduate students.

The men admitted were selected from a group of fifty-six applicants and are graduates of twelve colleges and universities, ranging from Massachusetts Institute of Technology and Yale in the east to the University of Southern California in the west.

Graduate work is being offered in the fields of pulp and paper technology, the chemistry of sugars and cellulose, colloidal chemistry, wood technology, and microscopy, mechanics, and the technical bibliography of the pulp and paper industry.

An extensive library on pulp and paper chemistry and technology is being accumulated. At the present time current and back files of eighty-six technical publications have already been assembled in addition to a large number of books on pulp and paper and related fields.

The Johns Hopkins University, Baltimore, Md. The following series of lectures under the Dohme Foundation, conducted in conjunction with the National Fellowship plan, has been arranged for the scholastic year, 1930–31: October 20th, DR. E. K. RIDEAL, Cambridge, England; November 7th, DR. ARTHUR D. LITTLE, A. D. Little Company, Cambridge, Massachusetts; December 12th, DR. J. J. ABEL, The Johns Hopkins University; January 16th, DR. MARSTON T. BOGERT, Columbia University, New York City; February 20th, PROFESSOR K. FREUDENBERG, Heidelberg, Germany; March 20th, DR. WILLIAM CROCKER, Boyce Thompson Institute, Yonkers, New York; April 17th or 24th, DR. MOSES GOMBERG, University of Michigan, Ann Arbor, Michigan; May 8th, DR. CHARLES A. KRAUS, Brown University, Providence, Rhode Island; May 15th, DR. WILDER D. BANCROFT, Cornell University, Ithaca, New York.

Loyola College, Baltimore, Md. The faculty announces the appointment of EDWARD S. HAUBER, S.J., as professor of physical chemistry. PIERRE A. KLEFF, '28, and BERNARD C. MCGOWAN, '29, have been awarded fellowships in chemistry at

Holy Cross College, Worcester, Mass. W. HELFRICH has been appointed librarian of the chemistry library for the year 1930–31.

Marquette University, Milwaukee, Wis. MESSRS. LYNN D. WILSON and GERALD LAWTON have been awarded fellowships in the department of chemistry for the current year.

The staff members of the chemistry department are planning their third annual series of radio talks, to be broadcast over the Marquette University Radio Station, WHAD, dealing with "Triumphs of Research." Some of the topics treated in previous programs were: "Nitrogen, Its Capture from the Air," "Radium, Its Discovery and Segregation," "Coal and Its Manifold Products," "Bakelite, the Material of a Thousand Uses," "Alkaloids, the Allies of the Physician," "The Lazy Elements of the Atmosphere," "Making Aluminum Cheaply," "Automobile Lacquers," "Saccharine—Sweeter than Sugar," "Carborundum," "Water Softeners," "Prolonging the Supply of Gasoline," "Modern Lubrication," "Chromium Plating," and "Rust-Resisting Metals."

The Marquette Chemical Society, an organization of students particularly interested in chemistry has outlined an interesting series of monthly meetings. Addresses by prominent chemists, movies dealing with chemical operations, and inspection trips form a part of their program.

Massachusetts Institute of Technology, Cambridge, Mass. E. J. SALSTROM (Ph.D., California, 1930) and A. R. DAVIS (Ph.D., Harvard, 1930) have been appointed instructors in inorganic chemistry. Dr. Salstrom comes from the University of California where he has been a teaching fellow for the past two years. Dr. Davis has been an instructor at Harvard.

E. C. COLLINS, who received his doctor's degree from North Carolina in 1927, has been appointed research associate in physical chemistry. Dr. Collins has taught for the last three years at the Teachers' College at Johnson City, Tennessee.

New York University, New York, N. Y. *Science Service* announces that teachers from New York University are to commute by airplane to other cities this winter in order to conduct extension courses. The experiment will be tried by the faculty of the School of Education at the University, officials of the school have announced. An airplane will be used for the teachers four days each week.

Four instructors will be carried by the plane each day to cities not readily reached from New York by railway or automobile. Leaving New York, the pilot will stop at each city where one of his passengers has a teaching engagement, and the next morning he will return to pick up the passengers and return them to the University in time for their day's work there.

Ohio Northern University, Ada, Ohio. DR. R. C. GIBSON (University of Michigan) has been appointed assistant professor of chemistry at this university. He will have charge of the division of analytical chemistry.

The Ohio State University, Columbus, Ohio. MR. SAMUEL HOYT addressed the Columbus Section of the American Society of Steel Treating on October 14th. His subject was "Tungsten Carbide." Mr. Hoyt is a metallurgist with the General Electric Company of Schenectady.

The new graduate assistants in the department of physiological chemistry are: WALTER C. AULT (Ohio State University); S. C. ELLIS (Wittenberg College); DONALD C. PRESTON (Wittenberg College); and SAM ROSENFELD (Ohio State University).

Professor CLAYTON S. SMITH, chairman of the department of physiological chemistry, attended the meeting of the American Association of Medical Colleges in Denver from October 12th to 14th.

The department of physiological chemistry now has a separate section for biochemists. In the past the biochemists and medical students have been in the same section and same laboratories. DR. HELEN L. WIKOFF will be in direct charge of the course.

MR. MAURICE E. HULL is a graduate assistant in the department of agricultural chemistry. After receiving the degree of bachelor of science in agriculture last December, Mr. Hull was extension assistant in soils for the remainder of the year.

PROFESSOR JAMES R. WITHROW, chairman of the department of chemical engineering, has been made a member of the advisory committee of committee C-7 on lime manufacture for The American Society of Testing Materials of Philadelphia.

MR. LAURENCE C. MAPEL (B.Ch.E., '23) is in charge of experimental research work and also development work at The O'Brien Varnish Company, South Bend, Indiana. MR. HARVEY GREER (B.Ch.E., '29) is a chemical engineer with The Goodyear Tire and Rubber Company at Akron, Ohio. DR. FESTUS L. MINNEAR (Ch.E., '30) is now a member of the technical staff of the Kimberly Clark Paper Company of Neenah, Wisconsin. MR. EDWIN W. MANN (B.Ch.E., '18) has been made a member of the staff at Rose Polytechnic Institute, Terre Haute, Indiana. RALPH HERBERT WING (M.Sc., Ch.E., '30) has accepted a position in the Department of Chemistry at Howard College, Birmingham, Alabama. MR. E. W. WALKE (B.Ch.E., '28) is manager of the pill and tablet department of the Walkerville, Ontario, plant of the Parke, Davis Company.

DR. HOWARD E. FRITZ (Ch.E., '23) is now chief engineer, chemical engineering division, mechanical rubber goods department of the B. F. Goodrich Company at Akron, Ohio.

PROFESSOR JESSE E. DAY, of the department of chemistry, addressed the Dayton Chemists' Association on September 5th on the "Catalytic Oxidation of Carbon." He also addressed the Ohio Fire School on September 18th on "The Chemistry of Fire."

Twenty-two of the papers presented at the Cincinnati Meeting of the American Chemical Society were given by a total of fourteen former graduates, three graduate students, and five professors—these representing the various chemical interests on the campus. The Ohio State Luncheon at the meeting held on September 11th was attended by sixty-seven representatives of this university. PROFESSOR WILLIAM MCPHERSON, president of the A. C. S. and dean of the graduate school of the university, was the principal speaker for the occasion. DR. W. C. GANGLOFF, of the Drackett Chemical Company, was in charge of arrangements.

MR. J. E. UNDERWOOD (Class '13) is assistant manager of development and research with the Pennsylvania Salt Company of Philadelphia. MR. R. K. BERTY (Min. Engr., '23) is engaged in ceramic research with the same company.

MR. GEORGE MACHWART, of the department of chemical engineering, was recently made an assistant professor in the department of chemistry of the University of Maryland. Mr. Machwart held the U. S. Bureau of Standards Coöperative Fellowship at Ohio State for the past two years.

The officers of the Columbus Section of the A. C. S. for the present year are: *Chairman*, C. B. MORREY; *Vice Chairman*, A. M. PATTERSON; *Secretary*, J. B. BROWN; *Councilors*, W. L. EVANS and H. E. OTTING.

Ohio Wesleyan University, Delaware, Ohio. The first of a series of fall trips for senior students in the department of chemistry of Ohio Wesleyan University was a visit to Cincinnati at the time of the meeting of the American Chemical Society. Seniors taking the trip were housed at special rates in one of the dormitories of the University of Cincinnati, through the efforts of DR. C. P. LONG of the Cincinnati Section. On Wednesday morning, Sept. 10th, a special breakfast for Ohio Wesleyan men was held at Hotel Gibson,

the students being the guests of the alumni and faculty present.

Registration in the advanced courses in chemistry at Ohio Wesleyan shows a large increase this fall, with a corresponding increase in the number of students who have selected chemistry as a major.

The Pennsylvania State College, State College, Penna. We learn from *Science* that MR. PHILIP D. ADAMS, instructor in the department of agricultural and biological chemistry, has resigned to accept a position as research biochemist at the Skin and Cancer Hospital of Philadelphia.

Purdue University, La Fayette, Ind. We learn from *School and Society* that MR. R. NORRIS SHREVE, consulting chemist of New York City, has been appointed to the faculty of the School of Chemical Engineering of Purdue University, to take charge of the work in organic technology.

Rose Polytechnic Institute, Terre Haute, Ind. PROFESSOR A. T. CHILD, who has been absent on leave during the past year, has returned and has resumed his activities at the Institute. Professor Child has spent the year in Europe and has been especially engaged in studying the details of operation of a number of chemical manufacturing plants in Belgium, France, Italy, and Germany. He has chiefly interested himself in those industries having to do with high-pressure synthesis and with the low-temperature distillation of coal.

During his absence Professor Child's work has been cared for by MR. ROBERT C. KINTNER of the chemical engineering staff of Ohio State University. Mr. Kintner has returned to the university and has resumed his work toward his doctorate there.

MR. EDWIN W. MANN (B.Ch.E., Ohio State University) is at the Institute this fall as instructor in general chemistry and in qualitative and quantitative analysis.

PROFESSOR JOHN WHITE, head of the chemical engineering and chemistry department at this Institute, has recently been chosen acting president of the Institute in succession to PROFESSOR JOHN B. PEDDLE who was forced to resign owing to ill health.

Rutgers University, New Brunswick, N. J. DR. WILLIAM THORNTON READ, recently appointed dean of the newly organized School of Chemistry of Rutgers University, received his training at Austin College, The University of Texas, Harvard, and Yale, and earned the Ph.D. degree from Yale in 1921. He then served on the faculty at Yale until 1925, when he accepted the chairmanship of the department of chemistry of Texas Technological College, Lubbock, Texas. He comes to Rutgers directly after five years of successful teaching and administration at the Texas institution. Dean Read replaces PROFESSOR R. G. WRIGHT, whose resignation from the chairmanship of the department of chemistry became effective in June, 1930.

Dr. Read is serving on the program committee of the North Jersey Section of American Chemical Society.

DR. DELMAR L. COTTLE (Ph.D., Ohio State, 1930) has been appointed assistant professor of organic chemistry.

State University of Iowa, Iowa City, Iowa. The following members of the chemistry faculty attended the meeting of the American Chemical Society at Cincinnati in September; DR. J. N. PEARCE, DR. L. CHAS. RAIFORD, DR. G. H. COLEMAN, DR. STEPHEN POPOFF, and DR. JACOB CORNOG.

DR. C. N. OTT (Ph.D., Iowa, 1926), who has been employed by the Mid-Continent Oil Company of Tulsa, Oklahoma, has accepted a position in the Central State Teachers' College at Edmond, Oklahoma. DR. G. W. THIESSEN (Ph.D., Iowa, 1927), who has been at Geneva College, Beaver Falls, Pa., is now in the chemistry department of Monmouth College, Monmouth, Illinois.

Union College, Schenectady, New York. DR. EGBERT KING BACON has joined the chemistry staff at Union College, coming from Brown University where he has been instructor in chemistry since 1926. Dr. Bacon received both his undergraduate and graduate degrees at the University of Michigan and was also instructor at Michigan before going to Brown. He is especially interested in colloid chemistry. At Union he will assist with the work in general and physical chemistry.

University of Arizona, Tucson, Ariz. DR. ERNEST ANDERSON, head of the department of chemistry, is on sabbatical leave the first semester of this year. He is carrying on his research at the University of Wisconsin.

MISS LOUISE OTIS received her doctor's degree from Northwestern University in June and is now a member of the chemistry staff of this university.

DR. ALEXANDER W. BOLDYREFF from the University of Michigan has been appointed to fill the place left vacant in the department when DR. T. F. BUEHRER transferred to the department of agricultural chemistry.

DR. L. E. ROBERTS returned to the department in September from Germany where he had devoted the preceding seven months to the study of physical chemistry.

MR. JACK CROWDER, who received his master's degree from this institution this spring, now holds a fellowship in the department of chemistry of Yale University. He is working toward his Ph.D. degree.

MR. JOHN MRGUDICH received his master's degree from Arizona in June and accepted a fellowship in the chemistry department at the University of Illinois, where he is beginning work toward a Ph.D. degree.

HOMER STAVELY and FLOYD RUSSELL, who were fellows in the department last year, now rank as assistant instructors.

Those holding fellowships in the department this year are as follows: GEORGE BAZZETTA, AUGUST W. ZAHNER, and LOUIS TOWLE (all B.Sc., University of Arizona, 1930) and WILBUR GARY (A.B., University of Florida, 1928).

University of Cincinnati, Cincinnati, Ohio. At the 1930 commencement the Hochstetter Prize of $40, given annually for the best graduating thesis in chemistry and chemical engineering, was awarded to DAVID RICHARDSON for his "An Infra-Red Study of Ergosterol." Honorable mention was given to "A Study of Carburization Catalysis" by CHARLES E. POTTER.

The annual prize of $25 given by the Cincinnati (Radium) Chapter of Iota Sigma Pi for outstanding work in chemistry by a senior or junior woman student was awarded to LEORA STRAKA.

University of Detroit, Detroit, Mich. The faculty of the chemical department of this university has been increased this year by the addition of FR. GEORGE J. SHIPLE, S.J. He comes from the Jefferson Medical College of Philadelphia where he served last year as instructor in biological chemistry. Sophomore and junior pre-medical and pre-dental students will make up his principal classes at the University of Detroit this year. He has inaugurated a new course for pre-medical students which will probably involve physical advanced organic chemistry. One of the divisions of this course will include a study of hydrogen-ion concentrations and buffer solutions.

Fr. Shiple took his master's work in biochemistry at St. Louis University in 1918, and his doctorate in the same branch under DR. CARL P. SHERWIN at Fordham University from 1919 to 1922. Fr. Shiple's investigations centered around the part which the alpha amino acids, especially glycine, glutamine, and cystine, play in this chemical defense mechanism of the animal organism, namely, in serving as a means for the animal body to detoxicate benzoic acid, phenylacetic acid, and bromobenzene, respectively. The important discovery was made that the human body is able to synthesize not only glycine but also glutamine for detoxication pur-

poses, and hence does not have to depend upon obtaining these substances from its food. The nitrogen necessary for this synthesis is obtained from that fraction of the waste nitrogen which would otherwise appear as urea. These results were published in *The Journal of the American Chemical Society*, **44**, 618 (1922); and in *The Journal of Biological Chemistry*, **53**, 463 (1922). The researches on cystine and its derivatives appeared in *The Journal of Biological Chemistry*, **55**, 671 (1923); **59**, 675 (1924); **60**, 59 (1924); **73**, 607 (1927); *American Journal of Physiology*, **69**, 518 (1924); and in the *Proceedings of the Society for Experimental Biology and Medicine*, **20**, 46 (1922); **20**, 360 (1923); **21**, 45 (1923).

University of Florida, Gainesville, Fla. DR. R. C. GOODWIN has submitted his resignation as assistant professor of chemistry in order to accept the chairmanship of the department of chemistry of the West Texas Technological College at Lubbock, Texas. DR. C. B. POLLARD has been elected assistant professor of chemistry succeeding Dr. Goodwin. He received his Ph.D. at Purdue in June, 1930, having been a member of the staff of that institution for the past nine years.

DR. T. R. LEIGH, head of the department of chemistry, and DR. V. T. JACKSON attended the fall meeting of the A. C. S. in Cincinnati. Dr. Leigh is councilor for the Florida Section and Dr. Jackson is a member of the Senate of Chemical Education.

ASSISTANT PROFESSOR B. J. OTTE, curator of the department of chemistry, received the M.S. degree at the June commencement. Professor Otte succeeds Dr. Goodwin as secretary of the Florida Section, A. C. S.

University fellows in chemistry for the year are as follows: C. E. SPARKS (B.S., Georgetown College, 1930); H. A. MAST (B.S., Muskingum College, 1930); G. A. HAWKINS (B.S.E., Florida, 1929); M. L. MOORE (B.S., Florida, 1930); S. M. THRONSON (A.B., St. Olaf College); W. C. TUCKER (M.S., Florida, 1930). Messrs. Thronson and Tucker have been accepted as candidates for the Ph.D. degree following a recent ruling making it possible for this degree to be offered by the departments of chemistry and pharmacy of the university.

MESSERS. LLOYD E. WEST and WAYNE B. WENGER, both of whom received their M.S. at the close of the summer session, have been elected members of the staff of North Dakota State College, Fargo, N. D.

PROF. J. A. OGG, member of the chemistry staff of North Carolina State College, pursued work leading to the M.S. degree during the past summer.

F. H. BABERS (M.S., 1927), now research chemist for the Rockefeller Institute, spent his vacation in Gainesville.

W. E. BLACKBURN (M.S., 1930) has been elected assistant professor of chemistry at the Kentucky State Normal.

H. C. WINTER (M.S., 1930) has accepted a fellowship in chemistry at New York University, where he will pursue work toward his doctorate.

F. D. AYRES (B.S., 1930) has accepted a fellowship in chemistry at Northwestern, where he will pursue work toward his doctorate.

L. E. MCELDOWNEY (B.S., 1930) has accepted a fellowship in biochemistry at Emory University, Atlanta, Ga.

S. K. LOVE (B.S., 1927) received his M.S. degree in June and returned to his position as chemist in the Water Resources Laboratory, U. S. Geological Survey, Washington, D. C.

JACK HESTER (M.S., 1930) has gone to Rutgers University as a fellow in chemistry and will pursue work leading to the Ph.D.

University of Illinois, Urbana, Ill. Iota Sigma Pi, at its national convention held at Cincinnati at the time of the American Chemical Society meeting, elected DR. VIRGINIA BARTOW national president for the ensuing year. Miss

Bartow is a member of the inorganic staff of the chemistry department.

The Association of Illinois Chemists held a luncheon meeting in Cincinnati at the time of the A. C. S. meeting. There were about one hundred former and present Illinois chemists in attendance. DR. H. C. PORTER, president of the association, presided. He called upon PROFESSORS S. W. PARR, B. S. HOPKINS, W. A. NOYES, W. H. RODEBUSH, and several others to speak briefly. A short business meeting concluded the assembly.

DR. C. R. BREDON, who received his doctorate in biophysico-chemistry at Ames has joined the staff of the sanitary chemistry department. He will act as routine bacteriologist, and conduct research on the anerobic bacteria acting on cellulose and cellulosic substances.

Several changes in the senior staff of the department have been made during the past few months. DR. L. W. ELDER of the analytical division is now associated with the du Pont Ammonia Corporation. DR. J. H. REEDY was promoted from assistant professor to associate professor, and transferred from the inorganic division to the analytical division. DOCTORS M. J. COPLEY, J. C. BAILAR, and L. L. QUILL were promoted from the rank of instructor to that of associate. Dr. Copley will teach thermodynamics and electrochemistry in place of PROF. T. E. PHIPPS, who is on leave of absence this year. He will also assist in the inorganic teaching work. DR. C. W. STILLWELL has been added to the inorganic staff with the rank of associate. DR. E. J. SHAW has been appointed to the staff as instructor, and will spend part of his time teaching inorganic and part teaching the laboratory courses in physical chemistry. ASSISTANT PROFESSORS R. C. FUSON and R. L. SHRINER have been promoted to the rank of associate professor. DR. C. S. MARVEL is now a full professor of organic chemistry. DR. VINCENT DU VIGNEAUD, an associate in physiological chemistry this past year, has been made an assistant professor.

The new chemistry annex building is rapidly nearing completion. The exterior work on the building was completed in the early part of September. The contractors were favored by fair weather, and now that the roof is finished, the task of finishing and equipping the interior of the new building can continue without delay. The tunnel joining the old chemistry building and the annex has been completed. It is planned, tentatively, to start using the annex at the beginning of the second semester.

PROFESSOR T. E. PHIPPS of the physical chemistry division, has been granted a Guggenheim Fellowship and, on leave of absence from the university for the year, is studying at the present time at Hamburg with PROFESSOR STERN.

University of Maryland, College Park, Md. An evening course in colloidal chemistry is being conducted at the Pharmacy School in Baltimore this year by the department of chemistry, on Tuesdays and Thursdays. DR. E. G. VANDEN BOSCHE of the chemistry staff of the School of Pharmacy is in charge. The course opened on October 2nd and will continue throughout the year. It is of graduate credit grade, but is open to any student having necessary prerequisites who desires an opportunity for advanced study.

University of Michigan. We learn from the *News Edition* of *Industrial and Engineering Chemistry* that J. J. THOMPSON and U. O. OAKDALE, candidates for the Ph.D. degree in this university, have received jointly first prize, an award of $100, in the American Pharmaceutical Manufacturers' Association contest. The basis of the award was an article by these two students entitled "A General Method for the Determination of Halogens in Organic Compounds," published in the **March, 1930,** issue of the *Journal of the American Chemical Society.*

University of Missouri, Columbia, Mo. DR. H. SCHLUNDT was called recently to the Eastern States to continue his investigation on radium poisoning.

DR. and MRS. A. E. STEARN spent the summer traveling in Europe, visiting in Belgium, France, Germany, Holland, and England. They attended the International Congress of Microscopic Biology held at the Pasteur Institute in Paris, and the National Hygiene Exhibits in Dresden, Germany.

DR. JAMES R. LORAH, assistant professor of industrial chemistry, was with the Skelly Oil Company during the summer.

MISS ZELLA VON GREMP (B.A., 1925, and M.A., 1930, University of Missouri), is assisting in general chemistry and is also a candidate for the Ph.D. degree.

MR. CARL HELMERS, who received his Master's Degree in August, has returned after a holiday in the Ozarks. He is registered as a candidate for the Ph.D. degree.

MR. WILLIAM BYLER (A.B., Warrensburg), now a candidate here for the M.A. degree, is serving as lecture assistant in inorganic chemistry. MISS BONNIE A. BRUNER (B.A., 1930, University of Missouri) is an assistant in inorganic chemistry and a candidate for the Master's Degree.

MR. ARTHUR SHAEFER (B.A., University of Missouri, 1930) is pursuing graduate work in the department of organic chemistry as a candidate for the M.A. degree and is assistant in organic chemistry.

MR. FRANK BRUNER (A.B., Doane College, Crete, Nebraska) is assistant in inorganic chemistry and also candidate for the Ph.D. degree.

MISS JEAN FREELAND (B.A., Maryville State Teachers' College, 1925) is assistant in inorganic chemistry and is also a candidate for the Master's Degree.

University of New Mexico, Albuquerque, N. M. DR. JOHN D. CLARK, professor of chemistry, spent the summer in Europe, and while there attended the Achema Ausstellung, at Frankfort, Germany.

PROFESSOR VEON C. KIECH has been granted a leave of absence for a year to finish his graduate work at Stanford University.

MAYNARD L. BOWEN and S. B. LIPPINCOTT have been appointed as instructors in the chemistry department.

University of Oregon, Eugene, Oregon. DR. A. H. KUNZ, Ph.D., University of Iowa, 1928, National Research Council Fellow at California School of Technology, 1929, and more recently with the du Pont Company, is in charge of the courses in analytical chemistry in the chemistry department at the University of Oregon. Dr. Kunz succeeds DR. RAYMOND D. COOL, who during the summer accepted a position with the University of Pennsylvania.

University of Wisconsin, Madison, Wis. *Science* announces that MR. J. ALFRED HALL, a graduate of the University of Wisconsin, has been appointed plant chemist in the Forest Products Laboratory, Madison, Wisconsin. He goes to Madison from Duke University, where he has been chief chemist of the chemical laboratory established under the Liggett and Myers Research Fellowships since 1928.

Wesleyan University, Middletown, Conn. PROFESSOR C. R. HOOVER resumed during the past summer his investigation of conditions affecting the growth of shad in the Connecticut River. This study was carried out under the auspices of the State Commission on Fisheries and Game.

Dr. Hoover and a corps of assistants during the summer also investigated the problem of industrial waste disposal in Connecticut, particularly those aspects of the general problem which involve the possibilities of stream pollution. This study also was carried on with the cooperation of state authorities.

DR. G. ALBERT HILL served as a reader in chemistry for the College Entrance

Examination Board. He later conducted the organic courses in the Harvard University Summer School.

Western Reserve University, Cleveland, Ohio. The graduate school of this university is conducting the following advanced courses in chemistry during the first semester this year: Experimental Study of Gases, Organic Synthesis, Chemistry of Foods, Recent Progress in Inorganic and Physical Chemistry, Atomic Structure in Relation to Chemical Problems, and Phase Rule. The hours of the courses are arranged for the convenience of persons employed in Cleveland industrial plants. The courses are being conducted by PROFESSORS OLIN F. TOWER and H. GRUENER, ASSOCIATE PROFESSORS H. S. BOOTH and R. E. BURK, and ASSISTANT PROFESSORS H. P. LANKELMA and F. HAVORKA. Special opportunity for research under the direction of the staff of the chemistry department is being offered in the fields of chemistry of gases, contact catalysis, the physical properties of liquids and solutions, especially specific heats, colloid chemistry, and synthetic organic chemistry.

FOREIGN

League of Nations Committee on Intellectual Coöperation. According to *School and Society*, the new permanent executive committee of the League of Nations, which is to follow and direct the development of international intellectual coöperation on behalf of the main League Committee on Intellectual Coöperation, will consist of MME. CURIE (Poland), SEÑOR CASARES (Spain), M. DESTRÉE (Belgium), SIR FRANK HEATH (Great Britain), PROFESSOR KRUSS (Germany), M. ROLAND MARCEL (France), PROFESSOR GILBERT MURRAY (president of the League Commission), M. PAINLEVÉ (president of the governing body of the Institute of Intellectual Coöperation), and SIGNOR ROCCO (Italy). This committee has been instructed to work out the details of the reorganization of the International Institute of Intellectual Coöperation and to take measures for its operation.

International Union of Pure and Applied Chemistry. According to *Science*, the following American chemists were appointed by the National Research Council to attend the tenth meeting of the International Union of Pure and Applied Chemistry which was held at Liège, Belgium, September 14th–20th: *Councilors*, CHARLES L. REESE, E. I. du Pont de Nemours and Co., Wilmington, Delaware, *chairman* of the delegation; EDWARD BARTOW, State University of Iowa, Iowa City; MARSTON T. BOGERT, Columbia University, New York City; JAMES B. CONANT, Harvard University, Cambridge, Massachusetts; AUSTIN M. PATTERSON, Antioch College, Yellow Springs, Ohio; CLAUDE S. HUDSON, U. S. Hygienic Laboratory, Washington, D. C.; *delegates*, C. A. BROWNE, U. S. Bureau of Chemistry and Soils, Washington, D. C.; J. V. N. DORR, Dorr Company, 247 Park Avenue, New York City; JOHN B. EKELEY, University of Colorado, Boulder, Colorado; GUSTAVUS J. ESSELEN, Boston, Massachusetts; WILLIAM LLOYD EVANS, The Ohio State University, Columbus, Ohio; JOEL H. HILDEBRAND, University of California, Berkeley, California; J. R. M. KLOTZ, American Cyanimid Company, New York City; G. M. NORMAN, Hercules Powder Company, Inc., Wilmington, Delaware; ALEXANDER SILVERMAN, University of Pittsburgh, Pittsburgh, Penna.

British Association for the Advancement of Science. *Chemistry and Industry* reports that the annual meeting of this association opened at Bristol on September 3rd under the presidency of PROFESSOR O. F. BOWER, F.R.S. An address on "A State Experiment in Chemical Research" was given by the president of the chemistry section, PROFESSOR G. T. MORGAN, F.R.S., director of the Chemical Research Laboratory at

Teddington, and chairman of the London section of the Society of Chemical Industry.

The Faraday Society. According to *The Chemical Age*, this society held a general discussion on "Colloid Science Applied to Biology" in the laboratory of physical chemistry, Cambridge University, from September 29th to October 1st. SIR WILLIAM HARDY introduced a discussion on "Equilibrium in Protein Systems" and SIR F. GOWLAND HOPKINS spoke on "The Structure of Living Matter."

The Institute of Metals. In the course of the annual autumn meeting of the Institute at Southampton, England, September 9 to 12, 1930, the Ninth Autumn Lecture was given by DR. D. HANSON, professor of metallurgy at the University of Birmingham. Dr. Hanson's subject was "The Use of Non-Ferrous Metals in the Aeronautical Industry."

Science Museum, South Kensington. *The Chemical Age* has announced that the new conference hall added to the Science Museum is now almost completed and will be used for scientific lectures during the coming winter. It will hold an audience of 200, and is well equipped for physical and chemical demonstrations.

University of Leeds. *The Chemical Age* states that DR. FREDERICK CHALLENGER, for the past ten years senior lecturer in chemistry at the University of Manchester, has been appointed to the chair of organic chemistry in the University of Leeds. Dr. Challenger has done considerable research in connection with aromatic organo-metallic and metalloidal compounds, including the orienting influence of the organic group, the sulfur compounds of shale oil, and the mechanism of mold fermentations.

The Public Library System of France. *School and Society* reports through *The Christian Science Monitor* plans for reorganizing the public library system of France by establishing a central library service attached to the Ministry of Public Instruction. The proposal of a special commission on libraries is that in the principal town of each of France's eighty-nine departments a collection of books and current periodicals served by a central bureau should be established. In recent years, France has spent less than 20,000,000 francs annually for all her libraries, of which only about 6,000,000 francs have been available for the purchase of books and subscriptions to periodicals. The project for reorganization of the libraries is largely due to the efforts of M. ROLAND-MARCEL, formerly head of the Bibliothèque Nationale in Paris. Public libraries were established in connection with primary schools in France as early as 1862, but often they have not been made really attractive to the reader. Almost the only function of many reading rooms has been to provide pupils in the schools with a place where they may study.

German Chemical Society. It is announced in *Giornale di Chimica Industriale ed Applicata* that at the April session of the German Chemical Society DR. NODDACK reported that the element rhenium, discovered by himself and his wife, has now been obtained in the form of a potassium salt of great purity. The chemical factories belonging to the Aschersleben Union of potassium plants near Leopoldshall, are producing monthly a considerable quantity of the salt containing 65% of metallic rhenium.

Kaiser Wilhelm Society for Advancing Science. It is announced in *School and Society* that DR. MAX PLANCK, emeritus professor of theoretical physics in the University of Berlin, has been elected president of the Kaiser Wilhelm Society for Advancing Science, Berlin, under the control of which are the various Kaiser Wilhelm Institutes.

Kaiser Wilhelm Society for Scientific Research. *Giornale di Chimica Indus-*

triale ed Applicata states that the Harnack House has been opened at Berlin-Dahlem in care of the Kaiser Wilhelm Society for Scientific Research, for the purpose of accommodating foreign scientists who come to Germany to study and as a headquarters for the society. Portions of the house will be at times at the disposition of other scientific societies for their sessions and social reunions.

University of Munich. According to a report in *School and Society*, the Institute of Physical Chemistry at the University of Munich, which is under the direction of DR. KASIMIR FAJANS, will share in a gift of the Rockefeller Foundation amounting to $375,000.

Indian Science Congress. *Nature* announces that the eighteenth annual meeting of the Indian Science Congress will be held in Nagpur, January 2 to 8, 1931. SIR MONTAGU SHERARD DAWES BUTLER, Governor of the Central Provinces, will be patron of the meeting, and LIEUT.-COL. R. B. SEYMOUR SEWELL, director of the Zoölogical Survey of India, will be president. The sectional president for chemistry will be PROFESSOR K. G. NAIK, professor of chemistry, Baroda College, Baroda.

Italian Association for the Advancement of Science. The nineteenth meeting of this association at Bolzano from September 7th–10th and at Trent from September 11th–14th has been announced in *Giornale di Chimica Industriale ed Applicata*. A paper on "Chemistry and Fertilization of the Soil in Italy" was read by DR. NICOLA PARRAVANO, a member of the staff of foreign editors of the JOURNAL OF CHEMICAL EDUCATION.

University of Rome. *School and Society* states that the Society of Friends of the University of Rome, which hopes to establish a Casa Americana or American section of the Students' House at the ancient university, held its first meeting on September 10th in New York City. The board of directors and founders include: JUSTICE JOHN J. FRESCHI and CHIEF JUSTICE FREDERIC KERNOCHAN of the Court of Special Sessions; PRESIDENT HIBBEN of Princeton University; DEAN ARCHIBALD BOUTON of New York University; DR. JOHN H. FINLEY; DR. JOHN GERIG of Columbia University; ROBERT UNDERWOOD JOHNSON and HENRY P. FLETCHER, former ambassadors to Rome; IRVING GOLDSMITH, PHILLIP LEBOUTILLIER, JEROME S. HESS, SAM LEWISOHN, WILLIAM GUGGENHEIM, and GUY VAN AMRINGE. The Italian ambassador at Washington, GIACOMO DEMARTINO, is chairman of the honorary committee. The following officers were elected at the meeting: *president*, JUSTICE FRESCHI; *vice presidents*, DR. GERIG and DEAN BOUTON; *chairman, national executive committee*, DR. JOHN H. FINLEY; *treasurer*, PHILIP LEBOUTILLIER; *assistant secretaries*, LUIGI DIONISI and JAMES S. HAUCK.

Museum and Institute of Chemical History. *The Chemical Age* states that the Soviet Government has decided to establish a Museum and Institute of Chemical History, having for its object the study of chemical science and industry, the spread of chemical knowledge and the furtherance of chemical progress in Russia.

South African Chemists Institute. *The Chemical Age* reports that at the annual meeting of this association, held in Johannesburg, PROFESSOR M. RINDL referred in his presidential address to the problem of finding employment for the many chemists who year by year are becoming qualified in the Union. Dr. Rindl expressed the conclusion that the profession has practically reached the saturation point in South Africa, as there has been little industrial development there during the last decade and present progress is slow.

National Bureau of Education, Union of South Africa. *School and Society* reports

the recent establishment of a national bureau of education in connection with the Department of Education of the Union of South Africa. The Bureau, it is said, will follow to some extent the plan of the U. S. Office of Education and similar English and German systems. Its function will be the collection, evaluation, and dissemination of "information concerning educational needs and actual progress in various directions." It plans to deal with educational questions on broad lines from a South African point of view, making available the experience gained in other countries.

Educational Developments in Sweden. We quote from *School and Society* the following abstract (through the *Times Educational Supplement*) of a report of the British Board of Education:

"Sweden has endeavored, by two successive pieces of legislation, to bring her educational system more into keeping with the needs of a nation which in the last 30 years has become rapidly industrialized.... The Parliamentary Act of 1918, by setting up various types of 'Practical Schools for the Adolescent' (in particular the whole-time higher primary schools), and by making part- or whole-time attendance at one of these compulsory between the ages of 13 and 15, has provided post-primary education for those unable to profit by secondary education. In the field of secondary education the legislation of 1927, by the partial adoption of the principle of the 'single educational ladder' in the state schools, and by reorganization of entrance and leaving examinations and of curricula, has sought to emphasize more than formerly the development of character and initiative, and to provide equal educational opportunity for all, irrespective of economic status, for girls as well as for boys, and in the country as well as in the towns.

"The main changes in the secondary system have been the throwing open to girls of the greater number of the state secondary schools (hitherto reserved to boys), and the taking over by the state of 54 secondary schools set up since 1904, with government aid, by the municipalities. There are at present 135 state secondary schools, as against 77 formerly. Swedish secondary education now normally consists of two parts; the *'realskola'* course leading to the *'realexamen'* at about the age of 17, and the *'gymnasium'* course, leading to the *'studentexamen'* at about the age of 20. The *'realexamen'* is a school-leaving certificate; the *'studentexamen'* qualifies for admission to the university."

University of Madrid. DR. E. MOLES of this university has spent the past few months on lecture tour in Argentina, Uruguay, and Chile. Dr. Moles, who is a member of the staff of foreign editors of the JOURNAL OF CHEMICAL EDUCATION, is expected to return to Madrid at the end of November.

Broken and Compressed Molecules May Explain Earth's Weight. Partly broken up and compressed molecules 2000 miles and deeper in the earth may account for this world's great weight, Dr. A. A. Bless, physicist at the University of Florida, suggested recently before the American Physical Society. The earth is much heavier than it would be if it were composed throughout of the materials found on its surface, and it is generally thought that this extra weight is supplied by an iron core. But Dr. Bless believes the dense material within the earth, whatever it is, would be lighter on the surface. Its molecules are ionized by the high temperatures, electrons being torn away from them, and thus the atoms are decreased in size, causing a sufficient increase in density to account for the observed mass of the earth, he explained.—*Science Service*

Recent Books

Henley's Twentieth Century Book of Recipes, Formulas, and Processes. GARDNER D. HISCOX, M.E. Eighth edition. The Norman W. Henley Publishing Company, 2 West 45th Street, New York City, 1930 xviii + 786 pp, about 60 illustrations. 21.5 × 13.5 cm. $4.00.

In a country where a copy of Young's "Distillation Principles" was once confiscated, and at least one teacher of high-school chemistry was discharged for imparting the rudiments of fermentation and distillation to his class, it may almost be dangerous to recommend a book which treats so ably of so many subjects between absinthe and zinc. The beverage section alone will insure a wide sale in certain quarters, although it is in no way a rival of the Bartender's Guide. Joking aside, this newly revised and enlarged edition of an old reliable book will be welcomed in many quarters—in some with unholy joy.

The editor has added a new chapter on laboratory methods which will greatly aid the lay reader in the compounding of the formulas given, and on any scale which he may desire to use. Many European authorities have been consulted, to the extent that one might wish to see more domestic references given. Still more modernization might have been achieved in this book. Under disinfectants, no mention is made of the dichlorobenzol preparations which are coming into common and effective use. Under ant destroyers, nothing is said of the thallium sulfate preparations which can now be purchased at any drug store. The use of fluorides as moth preventives, etc., goes unnoticed. A chemist and pharmacist should have been called in as assistant editors.

The book should be upon the reference shelf of the secondary-school chemistry teacher who is often called upon for formulas on short notice, much as the old-time schoolmaster was asked to solve tricky mathematics problems by those who wished to "stump" the teacher. Starting with these basic recipes, he can make many variations to suit individual needs. He can conceal a pardonable ignorance from those who still interpret the word chemist in the old English sense of the word.

R. E. BOWMAN

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Personal and Community Health. CLAIR ELSMERE TURNER, M.A., DR.P.H., Professor of Biology and Public Health in the Massachusetts Institute of Technology; Formerly Associate Professor of Hygiene in the Tufts College Medical and Dental Schools; Sometime Member of the Administrative Board in the School of Public Health of Harvard University and the Massachusetts Institute of Technology; Fellow, American Public Health Association; Major, Sanitary Corps, U. S. A. (Reserve). C. V. Mosby Company, St. Louis, Mo., 1930. 443 pp. 22 × 15 cm. $5.00.

The purpose of this book in the third edition does not deviate from the original intention of the writer, namely, to prepare a book on personal and community health for the student in the university, college, normal, or professional school.

The first portions of the book deal with the health of the individual and the maintenance of the individual's health through judicious habits of living and the building up of resistance against disease. The author has adequately discussed such topics as the hygiene of nutrition, the hygiene of the mouth, the hygiene of action, the hygiene of the central nervous system, and the hygiene of reproduction. The chapter dealing

with the fundamental facts of health maintenance is especially commendable. Although the diseases discussed in this particular chapter, by the very nature of this treatise, must be treated in only a fragmentary manner, the essential characteristics of such diseases as nephritis and diabetes are disclosed and the general regimen of treatment is indicated.

Part 2 of the book treats entirely of community health. The fundamental concepts of infection and immunity, and the relationship of these to communicable diseases are discussed.

Of special interest in a text of this kind are the chapters on food control, water supply, waste disposal, and the administration of public health to the various bureaus of state government.

The final chapter of the book deals with disinfection and disinfectants. In this chapter the author elucidates the fundamental principles which underlie disinfection and discusses some of the commonly used disinfectants. It is unfortunate, however, that nothing is said about the more modern types of disinfectants such as the organic mercury compounds which possess a high germicidal value and are used extensively among the laity.

To summarize, the author fulfils the purpose for which the book was written, that is, to present a general survey of personal health and its relation to the health of the community in its various ramifications. The style of the author is concise and easily comprehensible, and the text is free of typographical errors.

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Feeding the Family. MARY SWARTZ, PH.D. Third edition. The Macmillan Company, New York City, 1929. xvii + 459 pp. 18 plates. 14 × 19 cm. $3.75.

This volume is the third edition of a work which has already received deserved recognition and acclaim, but which now appears, thoroughly revised, refurbished with new illustrations, and equipped with newly arranged tables of food data. The plan of the author is two-fold—first, to consider the food needs of the different members of a typical family, and second, to guide the housewife in filling these needs. It is in every sense a book for the home, rather than a dietary guide for the institution or hospital. Two introductory chapters discuss briefly the chemistry of food and the physiology of digestion; then follow chapters treating of food for the adult man, the adult woman, the baby, children of various ages, adolescent youth, and the adult after fifty. Other chapters present menus, the cost of food, food plans and dietaries, and food for the sick. An appendix of a hundred pages contains extremely useful and well-arranged data, including a table on 100-calorie portions expressed in common household units, tables of vitamin values, etc.

The data contained in this book are up to date. In vitamin tables, the old vitamin B is relabeled vitamin (B + G), a terminology well recognized in America. A careful distinction is drawn between the factors of growth and of maintenance; increased emphasis has been placed on the daily use of foods which are sources of vitamins A and D, and of vitamins B and C for growing children. Nutritional science today emphasizes a diet not merely for maintenance but an optimum diet for higher mental and physical efficiency. Menus are arranged in the form of "a day's food plan"; the familiar calorie is retained as a unit, but used only as a tool; the fetish of calorie counting is largely avoided. Photographs of actual food materials grouped together show the quantities required to supply equivalent amounts of each of the vitamins—a wise substitute for the formal tables which characterize too many books on dietary science.

This book is not essentially a text, though it contains valuable reference material for both high-school and college classes in nutrition and dietetics. But

its use is in the home; it is written for the intelligent housewife, a demonstration that a guide on "What to Eat" need not be stepped down into popular slang or lose in sound scientific value when prepared for non-technical and extra-curriculum consumption.

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Intermediate Inorganic Chemistry. J. W. MELLOR, D.Sc., F.R.S. Vol. I. Longmans, Green, New York City, 1930. xx + 690 pp. 48 tables, 205 figures. 13 × 19.5 cm. $3.00.

The former title of this book was "Introduction to Modern Inorganic Chemistry." In the words of the author "some parts of this have been curtailed, some extended" and the name changed. The new edition is designed as an intermediate text between Mellor's "Elementary Inorganic" and "Modern Inorganic." The content of the book is best indicated by the chapter headings: 1. Physical Properties of Gases; 2. Chemical Nature of Air; 3. Ice, Water, and Steam; 4. Mixtures and Compounds; 5. Hydrogen, Oxygen, Nitrogen; 6. Atomic Hypothesis; 7. Composition of Water; 8. Revision of the Atomic Hypothesis; 9. Chlorine; 10. Acids, Bases, Salts; 11. Oxides of Carbon; 12. Energy and Matter; 13 & 14. Halogens; 15. Classification of Elements; 16. Alkali Metals; 17. Cu, Ag, Au; 18. Osmotic Pressure; 19. Ionic Hypothesis; 20 to 38. All common elements in order of Periodic System. Chapter 32 completes the discussion of the atmosphere started in Chapter 2. Chapter 2 is more historical and makes no mention of the rarer gases. The complete analytical data are left for Chapter 32.

The arrangement is different from that of the ordinary text in that the nonmetals, with the exception of the halogens, are studied in their respective periodic groups and are not all taken up before the study of the metals is started. It is difficult to see why the author has chosen to place "Colloids" under a chapter entitled "The Relations of Chlorine," and why some of the pure physical chemical theory such as Osmotic Pressure and the Ionic Hypothesis is left until Chapter 19, where it breaks into the continuity of the study of the elements according to the Periodic Arrangement, which was begun in Chapter 15.

The Phase Rule and Thermodynamics are briefly discussed in an excellent manner for this type of text. The electronic structure of matter has been largely omitted and valence is marked in Roman numbers or as H′ and Cl′ rather than the + and − signs.

The book is written in Mellor's characteristic pleasing style, which makes delightful reading. A set of questions, usually 10 or 15, follows each chapter.

While the material is presented in a manner simple enough for one who has never studied chemistry, there is still sufficient subject matter to hold the attention of a student who has had the customary course in high-school chemistry.

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Properties and Numerical Relationships of the Common Elements and Compounds. J. E. BELCHER and J. C. COLBERT, Assistant Professors of Chemistry in the University of Oklahoma. The Century Company, New York City, 1930. xii + 176 + vi + 160 pp. 33 illustrations. 21 × 27 cm. $1.75.

The authors make this statement in the preface: "This book contains all of the work included in *Experiments and Problems for College Chemistry* and the first thirty-three experiments in *Identification and Properties of the Common Metals and Non-Metals*." This latter work was reviewed in the JOURNAL OF CHEMICAL EDUCATION **6**, 1006 (May, 1929).

The purpose of the volume is to furnish "all the essential laboratory work of general chemistry in one manual." The

authors have fulfilled their mission to a very marked degree. The sixty-seven experiments cover the field of general chemistry very thoroughly. The work on chemical arithmetic, covering 28 pages and placed at the end of the experiments for the first semester, is very commendable. So frequently students in first-year chemistry have very hazy ideas of applying their knowledge of mathematics. The examples given should help to clarify the minds of the students with regard to the application of arithmetic to chemistry.

In addition to the comments made in the May, 1929, issue of THIS JOURNAL, the reviewer thinks a perusal of this manual will be profitable even though the teacher is satisfied with the results he is obtaining with a different manual.

The first 176 pages are intended to be covered in the first semester and the second portion, consisting of 160 pages, is intended to be covered in the second semester. It would perhaps cause less confusion if the pages were numbered from 1 to 336 instead of in the manner indicated above. Clarity would also be improved if the parts were given from I to V, instead of beginning the second semester's work with part I again.

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The Effects of Moisture on Chemical and Physical Changes. J. W. SMITH, B.Sc., PH.D., University College, London. With an introduction by DR. F. G. DONNAN. Longmans, Green and Co., London, New York City, Toronto, 1929. xii + 235 pp. 44 illustrations. 50 tables. 14 × 21.5 cm. Net price, $3.75.

This book should prove to be of the greatest value to those interested in catalytic reactions and the physical properties of substances. Dr. Smith has attempted to collect and correlate all the available data and theories relating to intensely dried systems.

The chapters, 24 in number, take up in order a general historical survey, gaseous reactions, such as the classic CO–O_2–CO_2, H_2–Cl_2–HCl, H_2–O_2–H_2O, NO–O_2–NO_2, and HCl–NH_3–NH_4Cl systems, solid-gas reactions, reactions between solids, reactions in non-aqueous solutions, decomposition of solids, physical properties and intensive drying, influence of traces of other catalysts, influence of an electrical field, etc. Not only are the various theories well discussed and all available data given, but much of the experimental technic necessary to success in such work is described in considerable detail.

Dr. Smith is to be commended for his able and much-needed contribution in a little-understood field.

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Die quantitative organische Mikroanalyse. FRITZ PREGL, Dr.Med. und Dr. Phil. H.C., O.Ö. Professor der Medicinischen Chemie und Vorstand des Medizinisch-Chemischen Instituts an der Universität Graz, Korrospondierendes Mitglied der Akademie der Wissenschaften in Wien. Third edition, Julius Springer, Berlin, Germany, 1930. xii + 256 pp. 51 figs. 15.5 × 23 cm. RM 19.80.

A detailed review of the third edition of a book so well known as this one is unnecessary. The second edition was translated into both French and English and a copy of this most important work is to be found in practically all of the libraries of chemistry. The rapid growth of the use of the methods of quantitative organic microanalysis and developments in the methods themselves made the third edition desirable.

The third edition follows closely the plan of the second. Professor Pregl confines himself chiefly to those methods of microanalysis which have been developed in his laboratory. The methods are described in minute detail, so that the beginner can make progress without other assistance and the work is admirably written for use as a textbook. The historical discussion is more com-

plete than in the second edition and some of this has been printed in small type. Various changes in the Pregl methods recommended by other investigators are discussed and criticized. Many of the chapters have been almost completely rewritten and the following methods appear which are not given in the second edition:

1. The Determination of Mercury, Microelectrolysis.
2. The Microacetyl Determination.
3. The Determination of the Molecular Weight:
   (*a*) By the method of Rieche,
   (*b*) By the method of Rast,
   (*c*) Of liquids by the method of A. Soltys.
4. The Micropolarimeter of Emil Fischer.

RALPH T. K. CORNWELL
SYLVANIA INDUSTRIAL CORP.
FREDERICKSBURG, VA.

Kurs obshi (Neorganicheskoi) Khimi. Course in Inorganic Chemistry. PROF. B. N. MENSHUTKIN. Third edition. Gosudarstvennoe Tekhnicheskoe Isdatelstvo, Moskva, 1930. 642 pages. Illustrated. 16.8 × 24.9 cm. 3 rubles, 90 kopeks.

The author of this book is professor at the Polytechnic Institute at Leningrad. He is known to the readers of the JOURNAL OF CHEMICAL EDUCATION because of his article on Lomonósov in the September, 1927, number. The third edition of his excellent and interesting textbook contains many diagrams, drawings, and tables, and seventy-five portraits of chemists among whom we note Moseley in his soldier's uniform; three Americans, Richards, Hall, and Langmuir; and nine Russians, Severgin, Lomonósov, Mendeléeff, Gess, Lovits, Yakobi, Klaus, Kurnakov, and Tamman.

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Laboratory Manual of General Chemistry. WILLIAM J. HALE, director, Organic Chemical Research, Dow Chemical Company, revised by WILLIAM G. SMEATON, Professor of General and Physical Chemistry, University of Michigan. The Macmillan Company, New York City, 1930. x + 530 pp. 17 figures. 19 × 13 cm. $1.60.

The purpose of the manual is to provide a series of experiments which can be coördinated with any standard textbook on general chemistry. In the words of the authors, "By judicious selection from the experimental material offered, an instructor can organize a practical course of elementary general chemistry to meet any reasonable requirement." The twelve reprintings indicate that they have been very successful in accomplishing this purpose.

The first chapter is taken up with detailed instructions for general laboratory procedures and practices. Chapters II to XVII contain experiments on the common elements and their usual reactions, with one chapter on ionization. Chapter XVIII gives a systematic scheme for the identification of negative radicals. Chapters XIX to XXVI outline experiments on the metals, the arrangement being similar to that in qualitative analysis. The final chapter contains notes on qualitative analytical procedure and a diagrammatic scheme for the identification of the cations. The appendix has seven tables of data for reference: I. Correction of Barometric Readings; II. Tension of Aqueous Vapor; III. Electromotive Series of the Metals; IV, V, VI. Solubilities; VII. Degree of Ionization, of Ionogens, Lists of Apparatus and Chemicals.

The pages are printed on but one side, leaving the other blank for the record of observations, so that no notebook is required. This is certainly a decided advantage to both student and instructor. However, in a number of experiments, the space allowed for the record must seem too limited to the average freshman.

In the first chapter under general directions, some of the details might be

omitted, such as the instructions in regard to side shelves, store room, distilled water, and microscope. Obviously such directions would apply to but *one* laboratory, and for all others would be useless.

The approach to the study of the metals by way of qualitative analysis is unusual. The general type of laboratory manual is inadequate in this part, and this arrangement would seem to be much better. Even if the student does not pursue a further course in analytical chemistry he will have a working knowledge of the reactions of the metals and their interrelation, *provided he has the time to complete the work outlined.* The amount of material given in the book is far too much to be covered in one course, and, as noted above, the authors do not intend it to be, but many laboratory directors experience difficulty in making a "judicious selection" without interrupting the continuity of the general scheme.

The directions are clear and explicit. The printing is plain and on paper that will hold ink.

The authors have wisely omitted giving directions for procedure which a student of only average intelligence can easily determine for himself. Perhaps this is the greatest merit of the book. The student must do more than record a column of one-word answers to a series of questions. He must do some thinking. He also will have opportunities to make "discoveries" for himself, instead of being told beforehand just what every result will be.

The book is also adequate for students in a second-year general chemistry laboratory course where such students do not expect to make chemistry their major, but desire some knowledge of the analytical and organic side.

F. H. EDMISTER

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Five Years of Research in Industry. 1926-30. A Reading List. Compiled by CLARENCE J. WEST, Director, Research Information Service for the Division of Engineering and Industrial Research, National Research Council. Division of Engineering and Industrial Research, National Research Council, 29 West 39th Street, New York City, 1930. 91 pp. 14.75 × 22.5 cm. $0.50.

"The primary purpose of this bibliography is to supply references to articles which provide answers to some of the following questions:

1. What are the conclusions of America's leaders of research?
2. What practical results are they achieving in their laboratories?
3. What is their opinion of coöperative effort in research as contrasted with individual effort?
4. How should the Research Department be organized?
5. What is the philosophy and method of operation of research laboratories in specific industries?

"A secondary purpose is to indicate those fields of research in which little or no work is being done."

. . . . . .

". . . the material has been selected with three main points in view: (1) Papers dealing directly with the value of industrial and scientific research, especially as they relate to a given industry. (2) Papers dealing with the development of a given industry or a particular industrial process. (3) Papers discussing the future of and the problems facing industry today.

"A careful survey of the papers falling under these three headings will give any one interested in a given field of research a picture of the past, present, and future of that field, and will enable him to evaluate the need for and the value of research, and the probable results to be achieved in the industry under consideration.

"No attempt has been made to list papers giving the results of individual

researches. Such papers have no place in a compilation of this kind. Should they be desired, reference to them may be found through the Engineering Index, Industrial Arts Index, *Chemical Abstracts*, and other indexes and abstract journals available in any large library. Reference to bibliographies on many special subjects covered in this compilation may be found in West and Berolzheimer's 'Bibliography of Bibliographies on Chemistry and Chemical Technology,' issued as Bulletins 50 and 71 of the National Research Council."

Both books and general articles are included, and references are listed under eighty-two main topics, alphabetically arranged. Invaluable for the professor of industrial chemistry and for the teacher of general chemistry who desires to include practical applications of chemical principles in his course. O. R.

BULLETINS

Filtration in Chemical Laboratories. A Handbook on Filtering Operations for the Chemist. CARL SCHLEICHER & SCHÜLL. New York City, 1927. 14.5 × 21.5 cm.

Uses of various (Carl Schleicher & Schüll) filter papers are indexed, not only under the various headings of different industries, but also under the names of the substances to be filtered, the ingredient to be determined, and the product to be analyzed.

O. R.

Digest of Legislation Providing Federal Subsidies for Education. WARD W. KEESECKER, Associate Specialist in School Legislation, Office of Education. United States Department of the Interior, Office of Education, *Bulletin*, **1930, No. 8.** U. S. Government Printing Office, Washington, D. C. (For sale by Superintendent of Documents.) 12 × 23 cm. $0.10.

College and University Extension Helps in Adult Education. L. R. ALDERMAN, Specialist in Adult Education, Office of Education. U. S. Department of the Interior, Office of Education, *Bulletin*, **1930, No. 10.** U. S. Government Printing Office, Washington, D. C. (For sale by Superintendent of Documents.) 12 × 23 cm. $0.10.

Study of Corrosive Action of Iodine. Studies on how iodine corrodes metals were reported at the recent meeting in Baltimore of the American Pharmaceutical Association by B. L. Meredith and W. G. Christiansen of Brooklyn, N. Y. Several alloys of metals that are resistant to most chemicals were experimented on. Both molten and vaporous iodine were used, but all the metals were corroded by the iodine, the investigators found.—*Science Service*

Stonelike Product, Maizolith, Made from Corncobs. Maizolith, a substance hard as stone and stronger than most kinds of wood, is one of the newest products of chemical magic working on cornfield wastes. It can be made from any part of the corn plant, but most advantageously from corncobs. It is one of the things that have been made by the chemists of Iowa State College at Ames, and has recently been undergoing tests on a semi-commercial scale at the U. S. Bureau of Standards. It is prepared by chemically digesting the corncobs, reducing them to a uniform jelly-like pulp in certain standard paper-mill machinery, and pressing the jelly in a mold. The resulting solid material is a dense, hard, bonelike substance, ranging in color from a golden tan to a deep ebony. It is somewhat stronger than the hardwoods, and is a good electrical insulator. It can be machined and polished into non-metallic gears, washers, panels, and other objects such as are now made from hard rubber and Bakelite. It is estimated that a commercial plant with a production capacity of five tons per day could manufacture it at a cost of about $240 a ton. The cost might be cut if it is manufactured as a by-product in other cornstalk industries. Its trade name, Maizolith, means into "corn-stone."—*Science Service*